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ABATEMENT OF MINE DRAINAGE POLLUTION BY UNDERGROUND PRECIPITATION

C. K. Stoddard

Pennsylvania Department of Environmental Resources

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October 1973

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16. Abstract

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Placement of the injection outlets, dispersion of the lime slurry, volume of water flowing, and direction of flow in the mine interior to other outlets are important controlling variables that greatly affect the efficiency of the sealing and neutralization of the outflowing acid mine water. (EPA)

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ABATEMENT OF MINE DRAINAGE POLLUTION BY UNDERGROUND PRECIPITATION

By

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Project 14010 EFJ
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Laboratory tests with synthetic acid mine water show the sealing effect of the gelatinous precipitate that forms when hydrated lime or powdered limestone is added in a simulated mine entry closed by a porous barrier.

Field tests were conducted in a recently abandoned coal mine. Hydrated lime and limestone slurries were pumped into the mine water behind rubble barriers through 2-inch steel pipes to test the laboratory findings. The outflow was observed at weirs attached to the ends of two, 12-inch diameter drain pipes. The results indicated that only temporary sealing of the outflow was achieved and that neutralization took place when the interior water flow conditions were favorable.

Placement of the injection outlets, dispersion of the lime slurry, volume of water flowing, and direction of flow in the mine interior to other outlets are important controlling variables that greatly affect the efficiency of the sealing and neutralization of the outflowing acid mine water.

Further field tests are required to demonstrate the practicality of the technique.

This report is submitted in fulfillment of Project 14010 EFJ (CR84), Contract WPRD-242-01, under the sponsorship of the United States Environmental Protection Agency and the Commonwealth of Pennsylvania, by Parsons-Jurden Division, The Ralph M. Parsons Company, 617 West Seventh Street, Los Angeles, California 90017.

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SECTION 1

CONCLUSIONS

PHASE I - LABORATORY PROGRAM

Laboratory investigations indicated that the underground precipitation method would be feasible to abate stream pollution by acid mine water drainage from abandoned coal mines. The laboratory investigations revealed that under proper flow conditions the precipitates formed within the mine will settle by gravity and remain in the mine while neutral or alkaline water will drain from the mine. The precipitates produced in the laboratory were found to be even bulkier than first postulated. In the tests, the precipitates that formed in the acid mine water, which flowed to the sand barrier in a simulated mine adit, completely sealed off or greatly reduced the water flow.

The laboratory phase confirmed the possibility of using underground precipitation to seal drainage channels for continuous underground neutralization, and for underground disposal of the precipitate.

PHASE II - FIELD DEMONSTRATION

Sealing

The flow of the mine water through the loose rubble barrier in the Driscoll No. 4 mine was stopped by the precipitates formed when hydrated lime and limestone were injected into the space upstream of the barrier.

The flow of water was stopped for only a short time; hence, the permanence of the plug is questionable.

Because of the tendency of the floc to settle to the entry floor at the injection points, the floc was unable to reach the higher portions of the rubble barrier as required. The No. 1 bulkhead created a pool of stagnant water behind the rubble pile and canceled the pressure head that would normally hold the floc against the rubble.

Additional laboratory work is required to substantiate the hypothesis that the gel or floc of iron hydrates and gypsum undergoes shrinkage and structural changes with age, which weaken or impair its effectiveness as a sealing agent.

The actual placement of a plug in a mine depends upon conditions developing after the outflow ceases, and provision for possible periodic replenishment of the sealing precipitates must be made. Maintaining the injection lines open and free is a design problem that must be worked out.

Continuous Neutralization

Continuous neutralization of the draining mine water was achieved as a by-product during the attempts to reestablish the seal.

During the tests, however, continuous neutralization of the outflowing mine water was not achieved because of the reversal of the flow of the water away from the No. 2 drain pipe at the slurry injection points when the outflow was reduced to a rate of 130 to 200 gpm.

The dye tests showed that the mine water in the area adjacent to the slurry injection points did not flow to the bulkhead drain pipes when the outflow was reduced to a rate of 130 to 200 gpm.

Point injections of the hydrated lime slurry were inefficient since good mixing was not achieved and stratification of the slurry and precipitates occurred on the entry floor.

Multipoint injection to achieve continuous neutralization would require the proper correlation of the factors of the settling rate of the floc, flow rate of the mine water to the outflow point, location of the area of contact between the lime slurry and mine water, and the rate of slurry injection. Changes in water inflow and outflow and conditions in the mine would require relocation of the injection points to obtain good results, and this could not readily be done in a sealed mine.

SECTION II

RECOMMENDATIONS

Further work in the laboratory or the field should be guided by information presented in this report, which shows that the physical layout of the mine and the water flow patterns are of major importance in effecting a seal and in providing continuous underground neutralization of the water. In most cases, continuous neutralization would best be accomplished outside the mine with standard chemical-processing equipment, and with adequate control of dosage rate to changing water flow and characteristics. The precipitated sludge could then be returned to the mine for disposal.

Plugging of mine water outflow by underground precipitation should be used only for carefully selected cases to shift the outflow to some other more manageable outlet.

Laboratory tests should be conducted to gather data about the effect of aging and possible dissolution of a plug by exposure to fresh acid water.

SECTION III

INTRODUCTION

Underground precipitation as a technique for elimination of pollution from abandoned coal mines is of interest from three standpoints: (1) filling of mine voids; (2) sealing drainage openings; and (3) continuous neutralization of effluent acid mine water. The use of underground precipitation in filling mine voids is based on forming the precipitates in the mine, thus providing an economic advantage over the cost of their return to the mine from a surface neutralizing installation. The use of underground precipitation in sealing drainage openings is advantageous as the precipitation can be carried to the outflow points and plug the openings similar to the "blinding" of a filter cloth. Finally, underground precipitation would be a means for continuous neutralization of effluent acid mine water without the concurrent problem of sludge disposal.

Under a contract with the Pennsylvania Department of Mines and Mineral Industries, Parsons-Jurden Corporation engaged in a study of underground precipitation in abandoned mines, resulting from the reaction of mine water with hydrated lime and limestone, to prevent mine drainage pollution. This work, described herein, was supported in part by a demonstration grant by the Federal Water Pollution Control Administration to the Commonwealth of Pennsylvania, under Title II, Section 6(a) of the Federal Water Pollution Control Act as amended by the Clean Water Restoration Act of 1966.

The laboratory work conducted as part of this study (covered in the Appendix) was performed by personnel at the Plymouth Meeting, Pennsylvania laboratories of G. & W.H. Corson, Inc., under subcontract to Parsons-Jurden.

The field tests covered in this report are summarized below, together with the chronology of the testing activities.

Chronology of the Field Tests

3/10/69 to 4/26/69	Mobilization and dewatering of mine portal entries
4/27/69 to 5/10/69	Entry rehabilitation - cleaning out and timbering, pumping

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Chronology of the Field Tests (Contd)

5/10/69 to 6/28/69	Timbering continues, hitches cut for No. 1 and No. 2 bulkheads; forms and rebars installed - pumping continues
6/28/69 to 9/24/69	Work suspended except for pumping to resolve need for No. 3 bulkhead and arrange new construction contract
9/24/69 to 11/7/69	All bulkheads completed
9/21/70	Authorization to proceed with field demonstration test received
10/5/70 to 11/3/70	Preparation of site, and setting up equipment for plugging and continuous neutralization tests
11/3/70 to 11/17/70	Plugging test in No. 1 west entry
11/18/70 to 11/22/70	Continuous neutralization test in No. 2 west and north entries
12/9/70 to 12/16/70	Replugging efforts in No. 1 west entry
12/16/70 to 12/17/70	Site dismantling

SECTION IV

PREPARATIONS AT THE MINE SITE

The workings of the Driscoll No. 4 Mine consist of a 4-1/2-foot coal seam that underlies an extensive hilly area. The seam dips to the northwest from the outcropping at the base of the south side of a hill that rises along the banks of Black Lick Creek at Vintondale, Pennsylvania (Figure 1). The mine first opened in 1906 and was considered mined out sometime in the 1950s, but it was reactivated in the early 1960s to work a new section along the western fringe of the older workings which are said to extend several miles from the portal in a northerly direction. Figure 2 is a view of the area immediately in front of the portal. A new portal was opened to the west of the original portal. In compliance with newer regulations covering coal mines, three entries branched out from the portal: the No. 1 west entry, north entry, and east entry (Figure 3). A fourth adit, the No. 2 west entry, branched off from the north entry at a point about 25 feet from the portal and paralleled the No. 1 west entry. The north and east entries connected with the old mine workings. The No. 1 and No. 2 west entries comprised the active mine.

In 1967, operation of the mine was discontinued, the pumps were removed, and the mine began to fill with water. The east entry was caved to prevent entry of personnel. The mine portal was also to be backfilled with 25 feet of noncombustible material to seal the mine against entry. However, this was not done so that the mine could be used as the field site for demonstration purposes reported here.

A field survey and a study of available mine maps led to the decision to use the No. 1 west entry for the water sealing demonstration. A rubble pile would be placed in the adit, to be sealed by the precipitate formed by pumping a slurry of hydrated lime and/or ground limestone into the mine water behind the rubble pile. Three concrete bulkheads would be required to control the water flow. It was also decided to use the No. 2 west entry and the north entry to test the possibility of continuously neutralizing acid mine water, and simultaneously eliminating the sludge disposal problem, by precipitating the mineral content from the water before it drained out and then allowing the sludge to settle into the lower portions of the mine.

A plan of the construction undertaken at Driscoll No. 4 is shown in Figure 4. The water level was lowered by pumping to permit repair of the portal. Steel rails and posts were installed for maximum safety. The north entry and the No. 2 west entry were propped up for safe entrance. The water level was lowered further to permit cleaning and the repair of the No. 1 west entry for a distance of 120 feet west of the portal. After the entry had been cleaned and repaired, emplacement of the rubble pile was started.

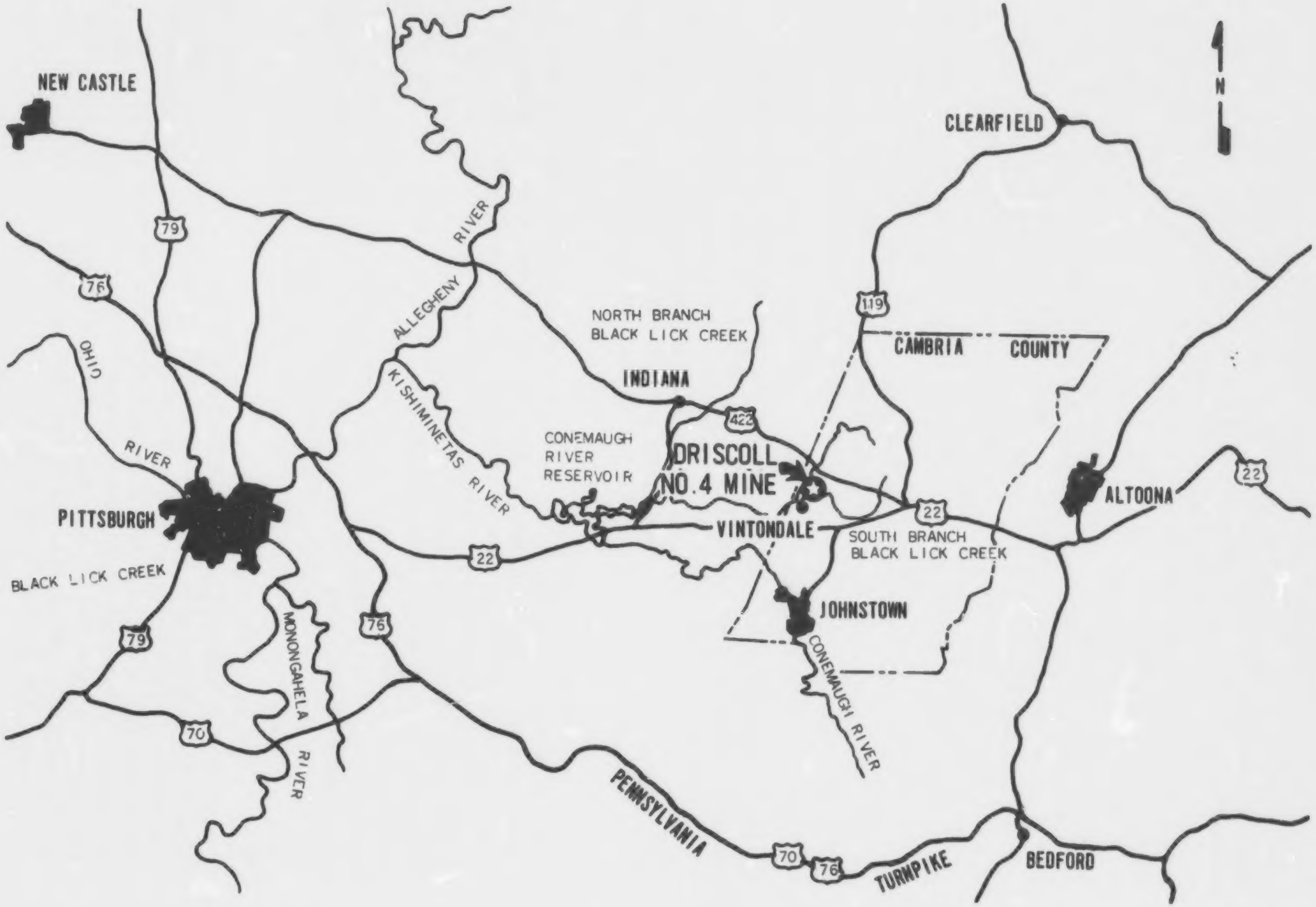

N
NEW CASTLE
CLEARFIELD
79
76
RIVER
ALLEGHENY
119
NORTH BRANCH
BLACK LICK CREEK
CAMBRIA
COUNTY
OHIO
INDIANA
422
KISHIMINETAS RIVER
CONEMAUGH
RIVER
RESERVOIR
DRISCOLL
NO. 4 MINE
22
ALTOONA
RIVER
PITTSBURGH
VINTONDALE
SOUTH BRANCH
BLACK LICK CREEK
BLACK LICK CREEK
JOHNSTOWN
MONONGAHELA
RIVER
CONEMAUGH RIVER
70
PENNSYLVANIA
TURNPIKE
BEDFORD

Figure 1 - Location of Driscoll No. 4 Mine

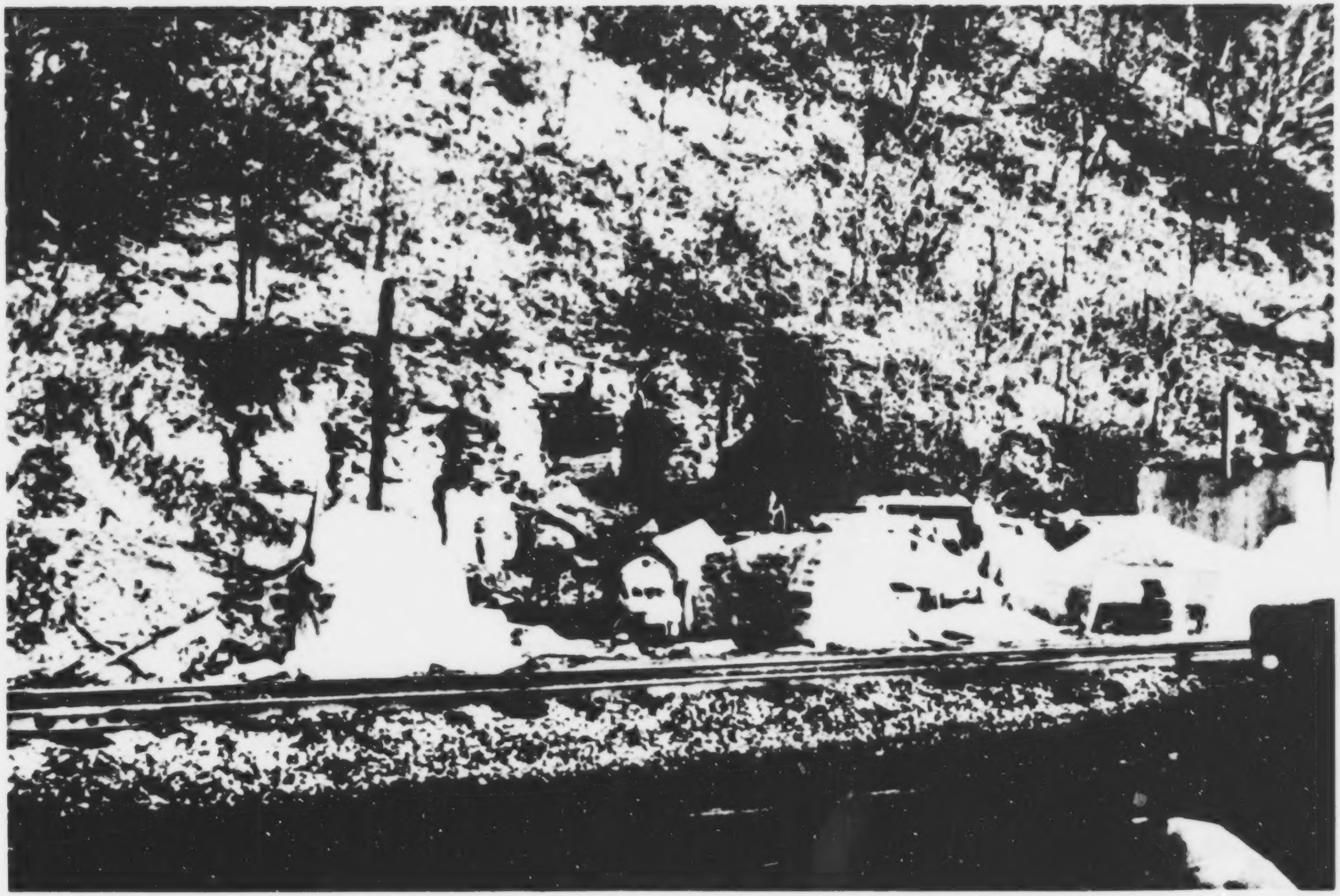


Figure 2 - Driscoll No. 4 Mine (View Looking North Toward the Mine Portal)

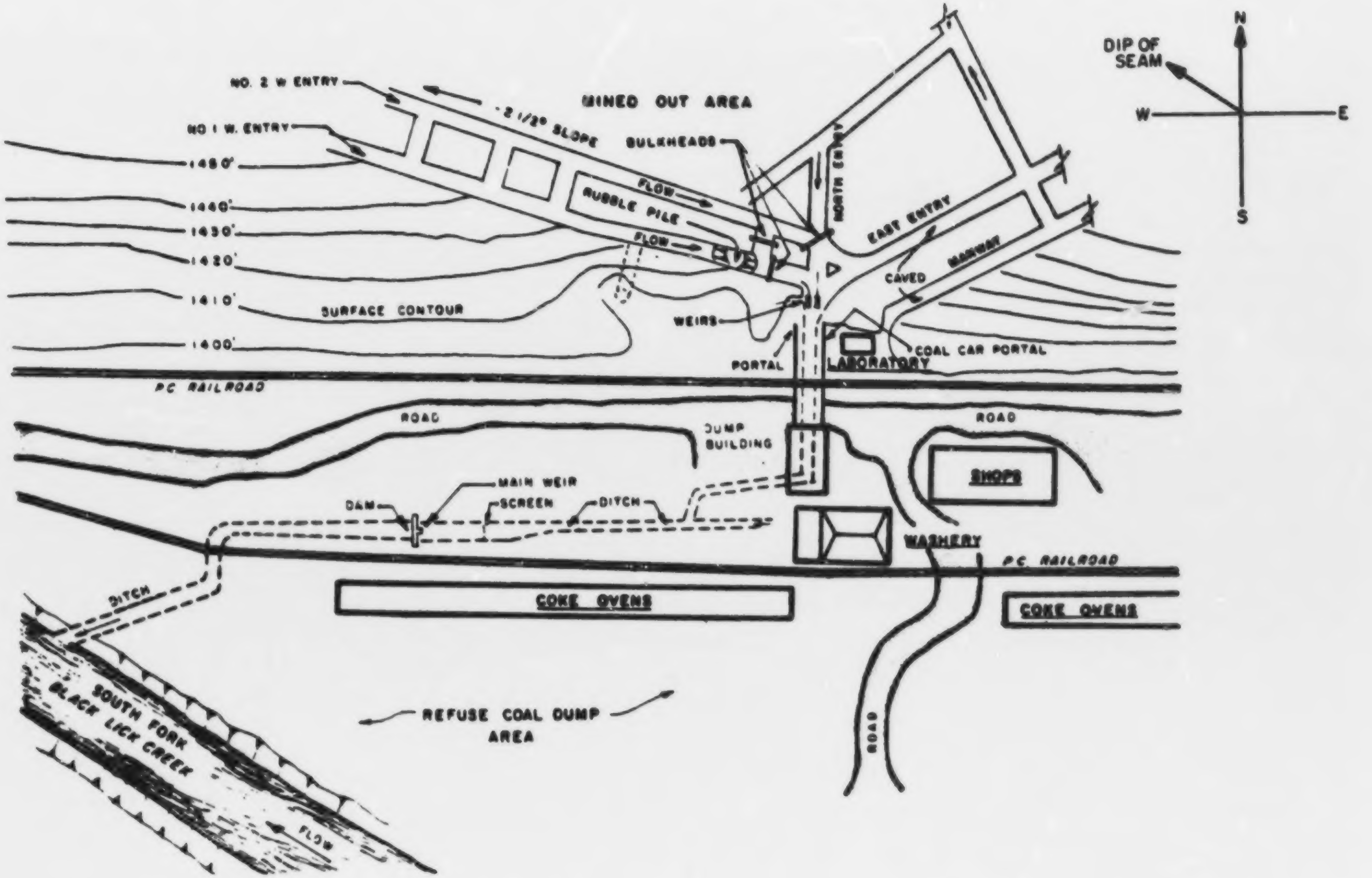

DIP OF SEAM
N
W
E
S
MINED OUT AREA
NO. 2 W ENTRY
NO 1 W. ENTRY
-2 1/2° SLOPE
BULKHEADS
FLOW
RUBBLE PILE
FLOW
NORTH ENTRY
EAST ENTRY
MANWAY
CAVED
WEIRS
PORTAL
COAL CAR PORTAL
LABORATORY
1480'
1440'
1430'
1420'
1410'
1400'
SURFACE CONTOUR
P.C. RAILROAD
ROAD
DUMP BUILDING
ROAD
SHOPS
MAIN WEIR
DAM
SCREEN
DITCH
WASHERY
P.C. RAILROAD
COKE OVENS
COKE OVENS
DITCH
SOUTH FORK BLACK LICK CREEK
FLOW
REFUSE COAL DUMP AREA
ROAD

Figure 3 - Plan of Surface and Mine Workings

Inert material consisting of broken slate, shale, and glacial till was placed by hand, using wheelbarrows and shovels. The entry was filled and compacted to produce a pile 25 feet long (as measured at the roof of the drift.) Three 2-inch steel pipes with pointed, slotted ends were driven through the pile, terminating 3, 6, and 9 feet, respectively, behind the top of the pile (Figures 4 and 5.) Following settlement of the rubble pile, the top of the pile was refilled and the toe reinforced with sandbags. The rubble pile was porous enough to permit water to drain through.

Three 2-inch injection lines were installed in the No. 2 west entry, terminating 90, 105, and 120 feet, respectively, behind the No. 2 bulkhead (described below.) Three similar injection lines were installed in the north entry, 50, 65, and 80 feet, respectively, behind the No. 2 bulkhead. All injection lines behind the bulkheads were Schedule 40 steel pipe, supported on wooden posts near the entry roof. Prior to the injection tests, the steel injection pipes were connected to plastic pipes at a point close to the outside face of the bulkheads.

Initial study of the Driscoll No. 4 Mine Layout indicated the need for bulkhead Nos. 1 and 2, which incorporated 12-inch drainage lines with valves. Bulkhead No. 1 was to be installed near the opening of the No. 1 west entry. This structure, with its 12-inch drainage line and valve, would control the water flow from the No. 1 west entry. Before constructing the bulkhead, the 25-foot-long rubble pile was to be placed in the entry about 10 feet behind the bulkhead. Under these conditions, the first cross-entry to the No. 2 west entry, on the right, would be upstream of the rubble pile and, therefore, would require no flow control.

Later in the study it was found that the rock near the opening of the adit was not sound enough to hold the bulkhead; hence the bulkhead position was moved back into the adit a sufficient distance to ensure sound rock and provide a watertight bulkhead. After moving the bulkhead back into the mine, the cross-entry opened downstream of the rubble pile, rather than upstream as originally conceived. Since this would provide a bypass for water flow around the rubble pile, the No. 3 bulkhead was required in the cross-entry.

The No. 1 bulkhead was located in the No. 1 west entry and provided with a 12-inch steel drainage pipe; and No. 3 was placed in the cross-entry, as shown in Figure 5. The three injection lines which were driven through the rubble pile extended through the No. 1 bulkhead. The No. 2 bulkhead was also provided with a 12-inch steel drainage pipe.

Six injection lines were installed, three in the No. 1 west entry and three in the north entry. The No. 3 bulkhead in the cross-entry was solid.

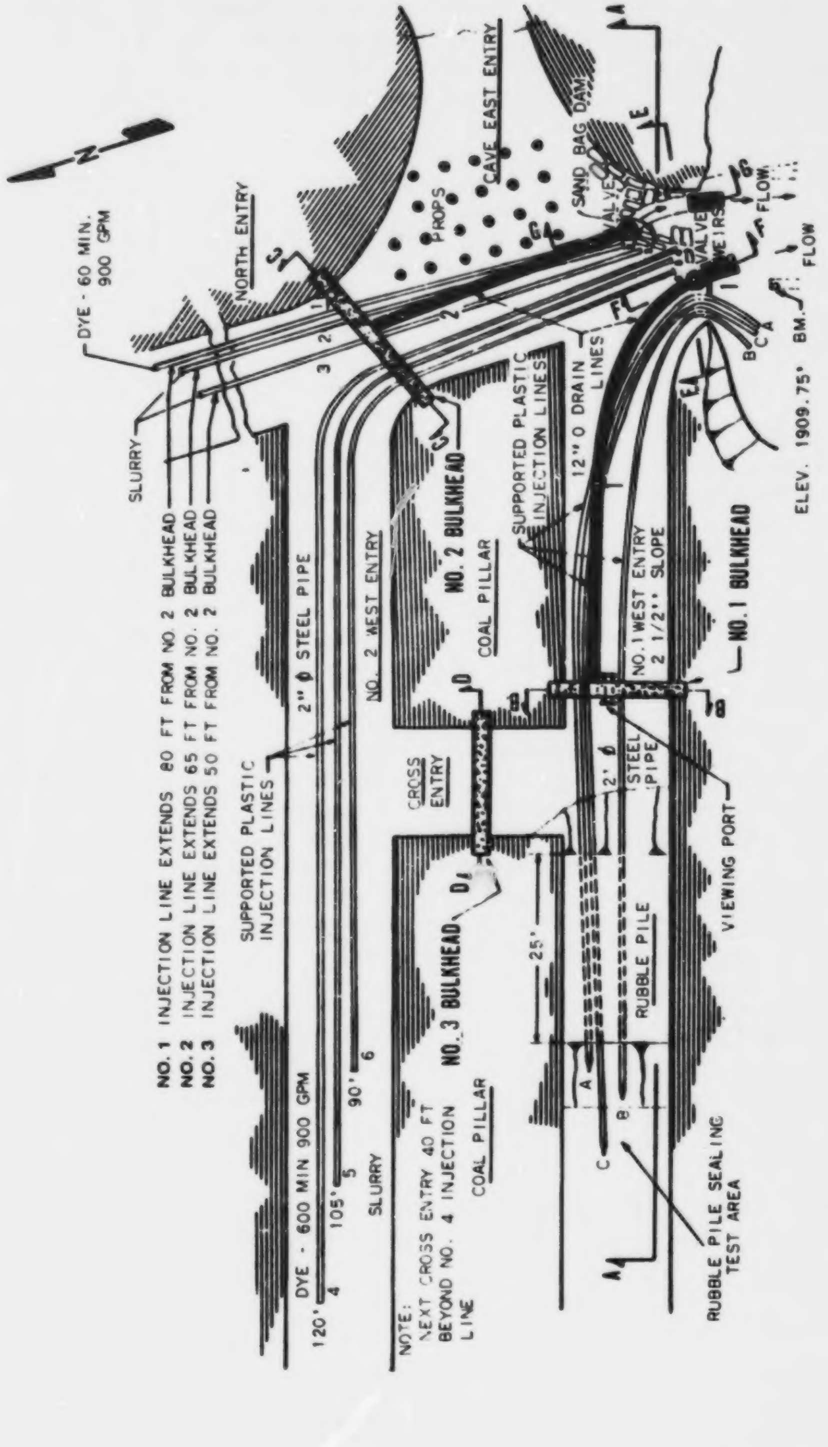

N
NO.1 INJECTION LINE EXTENDS 80 FT FROM NO. 2 BULKHEAD
NO.2 INJECTION LINE EXTENDS 65 FT FROM NO. 2 BULKHEAD
NO.3 INJECTION LINE EXTENDS 50 FT FROM NO. 2 BULKHEAD
DYE - 60 MIN. 900 GPM
SLURRY
NORTH ENTRY
PROPS
CAVE EAST ENTRY
SAND BAG DAM
VALVE
VALVE
WEIRS
FLOW
FLOW
ELEV. 1909.75' BM.
SUPPORTED PLASTIC INJECTION LINES
12" Ø DRAIN LINES
NO. 2 BULKHEAD
COAL PILLAR
NO. 2 WEST ENTRY
2" Ø STEEL PIPE
SUPPORTED PLASTIC INJECTION LINES
CROSS ENTRY
NO. 1 WEST ENTRY 2 1/2" SLOPE
NO. 1 BULKHEAD
2' Ø STEEL PIPE
VIEWING PORT
25'
RUBBLE PILE
NO. 3 BULKHEAD
COAL PILLAR
DYE - 600 MIN 900 GPM
120'
105'
90'
SLURRY
NOTE: NEXT CROSS ENTRY 40 FT BEYOND NO. 4 INJECTION LINE
RUBBLE PILE SEALING TEST AREA
1
2
3
4
5
6
A
B
C
D
E
F
G
A
B
C

Figure 4 - Plan of Bulkheads, Piping, Weirs and Portal

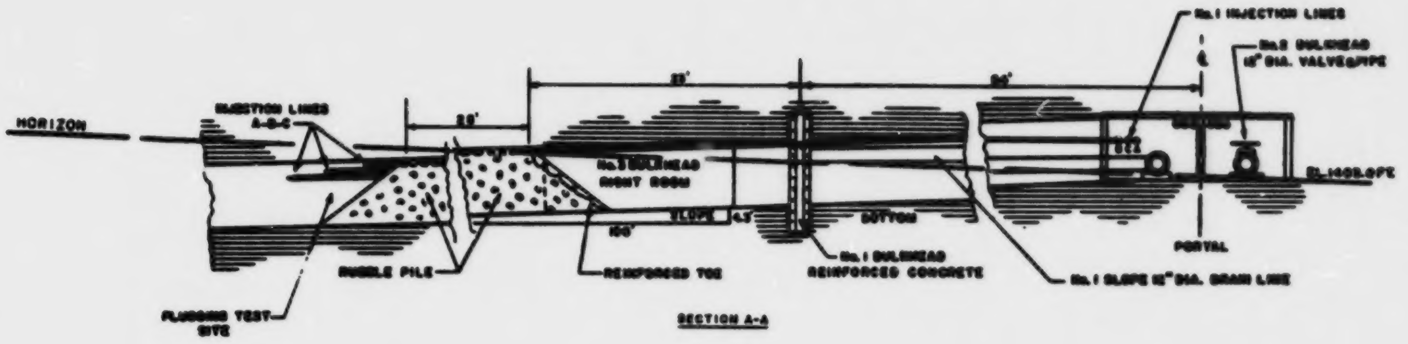

HORIZON
INJECTION LINES A-B-C
28'
No. 3 BULKHEAD RIGHT ROOM
SLOPE
4.5'
100'
BOTTOM
No. 1 BULKHEAD REINFORCED CONCRETE
No. 1 INJECTION LINES
No. 2 BULKHEAD 12" DIA. VALVE & PIPE
EL. 1408.0 FT.
PORTAL
No. 1 SLOPE 12" DIA. DRAIN LINE
RUBBLE PILE
REINFORCED TOE
PLUGGING TEST SITE
SECTION A-A

Figure 5 - Section Through No. 1 West Entry and Mine Portal

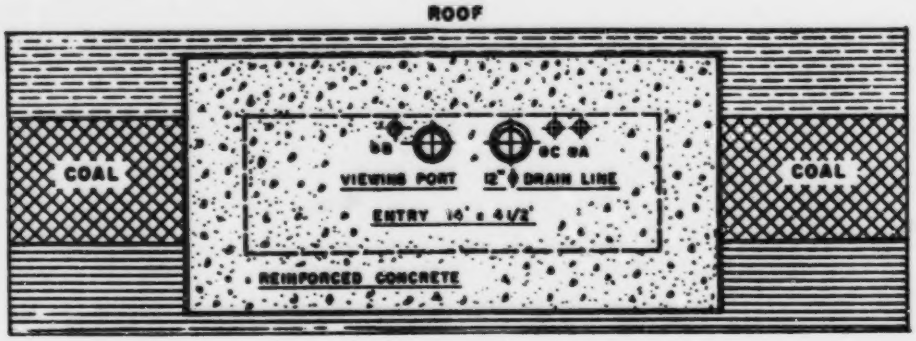
As mentioned above, the bulkheads were located where good ground conditions existed in the entries. Eighteen-inch-wide slots were excavated 24 inches into the side walls, floor, and roof of each entry to lock the bulkheads in place and provide a watertight seal. Concrete reinforcing bars were placed in the excavations, and injection lines and drainage lines were installed. Wood forms were set in place and concrete pumped into the form. Figure 5 shows a section in elevation through the No. 1 bulkhead, No. 1 west entry, and mine portal. Bulkhead details are shown in Figure 6.

Bleeder lines were placed in the back of the bulkhead excavations to bleed off air so that the entire excavated area would accept concrete. The 12-inch drain lines were extended from the No. 1 and No. 2 bulkheads out to the portal. Gate valves were installed on the ends of these lines to permit control of the flow through the two discharge points. The mine was then no longer accessible to personnel.

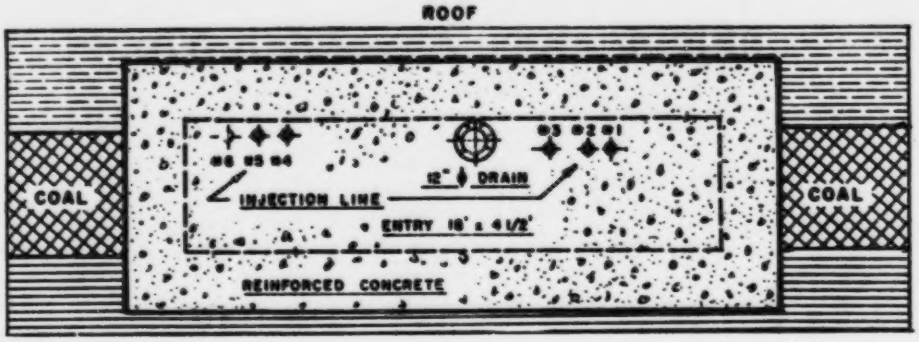
The 2-inch injection lines were capped temporarily to prevent water flow through them. The pumping was then discontinued, and the entry allowed to refill and drain through the two 12-inch drain lines. Some months later, when the preparations for the tests were started, it was found that a rock slide had occurred in the interim. To make the portal safe once again, it was necessary to remove several large chunks of rock from the brow of the portal and place additional timbering in the entries. The area from the portal back to the bulkheads was pumped out to permit access to the bulkhead faces. The 2-inch steel injection lines were uncapped and 2-inch plastic lines were attached and extended out to the portal. A clay core and sandbag berm was constructed at the portal to prevent flooding this area once again and to channel the water flow from the drainage pipes (Figure 7.) However, because of seepage from the caved east entry, it was impossible to keep this area from flooding.

One steel weir box containing a 30-degree V-notched plate was bolted to No. 1 drain pipe valve (Figure 8) and a second was placed several feet downstream of the No. 2 drain pipe valve (Figure 9.) The sandbag berm channeled the water from the No. 2 valve to the No. 2 weir box. Because of the large flow of water from the No. 2 drain pipe, it was necessary to cut the front plate of the No. 2 weir to produce a 12-inch rectangular weir. A 90-degree V-notched plate was inserted during periods of low flow. Additional views of the portal and weirs are shown in Figures 10 and 11.

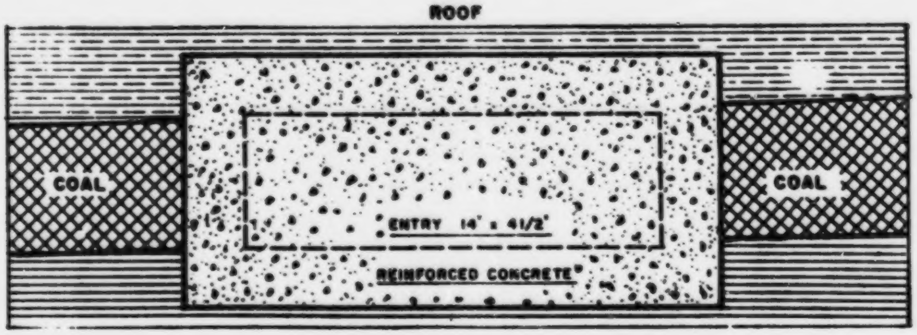
Water from the No. 1 and No. 2 drainage lines discharged to an existing drainage ditch that flowed into the south branch of Black Lick Creek (Figure 3.) The third weir, identified as the main weir, containing a 30-degree V-notched plate (Figure 12), was placed in this ditch. A trash-catching screen was installed about 50 feet upstream of this weir to prevent interference by floating debris.


ROOF
#B
#C #A
COAL
COAL
VIEWING PORT
12" ϕ DRAIN LINE
ENTRY 14' x 41/2'
REINFORCED CONCRETE

No. 1 BULKHEAD
SECTION B-B


ROOF
#6 #5 #4
#3 #2 #1
COAL
COAL
12" ϕ DRAIN
INJECTION LINE
ENTRY 16' x 41/2'
REINFORCED CONCRETE

No. 2 BULKHEAD
SECTION C-C


ROOF
COAL
COAL
ENTRY 14' x 41/2'
REINFORCED CONCRETE

No. 3 BULKHEAD
SECTION D-D

Figure 6 - Sections Through Bulkheads

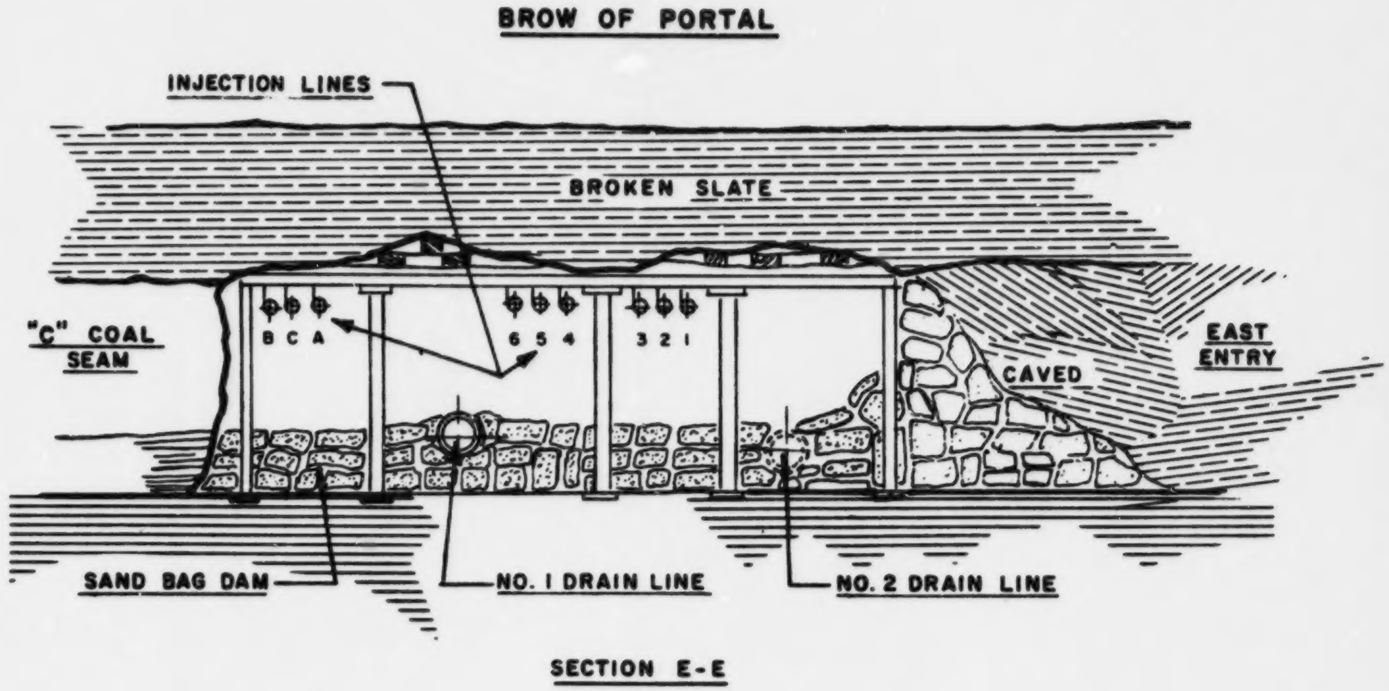

BROW OF PORTAL
INJECTION LINES
BROKEN SLATE
"C" COAL SEAM
B C A
6 5 4
3 2 1
EAST ENTRY
CAVED
SAND BAG DAM
NO. 1 DRAIN LINE
NO. 2 DRAIN LINE
SECTION E-E

Figure 7 - Section Through Mine Portal

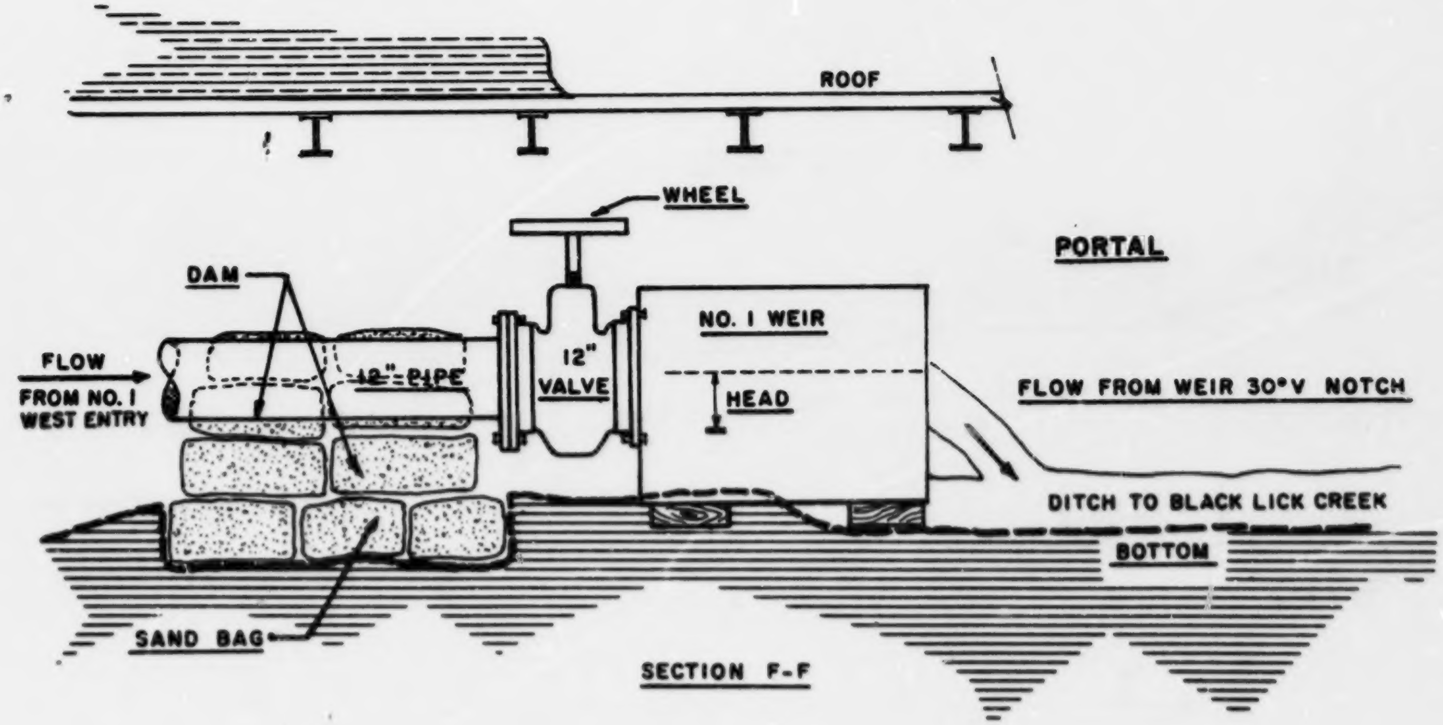

ROOF
WHEEL
PORTAL
DAM
NO. 1 WEIR
FLOW
FROM NO. 1
WEST ENTRY
12" PIPE
12"
VALVE
HEAD
FLOW FROM WEIR 30°V NOTCH
DITCH TO BLACK LICK CREEK
BOTTOM
SAND BAG
SECTION F-F

Figure 8 - Section Through No. 1 Pipe and Weir

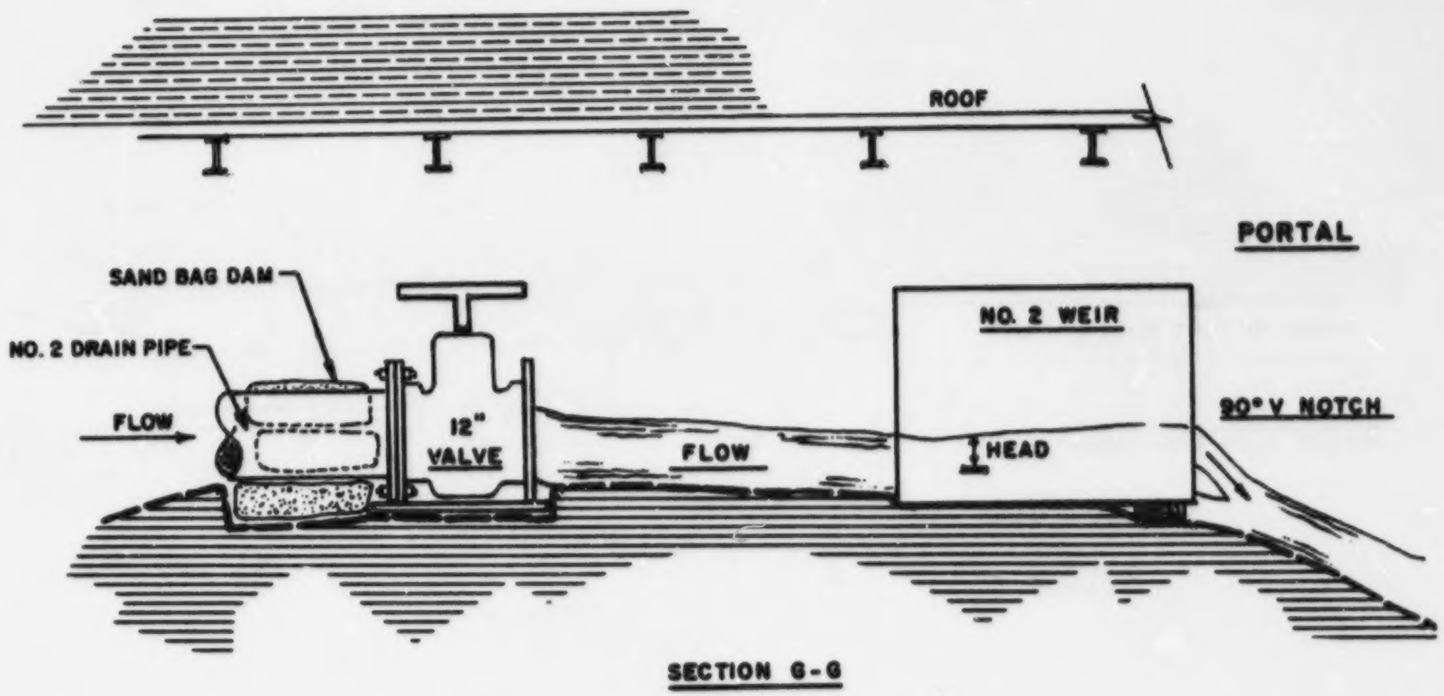

ROOF
PORTAL
SAND BAG DAM
NO. 2 DRAIN PIPE
FLOW
12"
VALVE
FLOW
NO. 2 WEIR
HEAD
90° V NOTCH
SECTION G-G

Figure 9 - Section Through No. 2 Drain Pipe and Weir

Figure 10 - Front View of No. 1 Weir (Entry to Mine Portal is to Left of Weir Box)

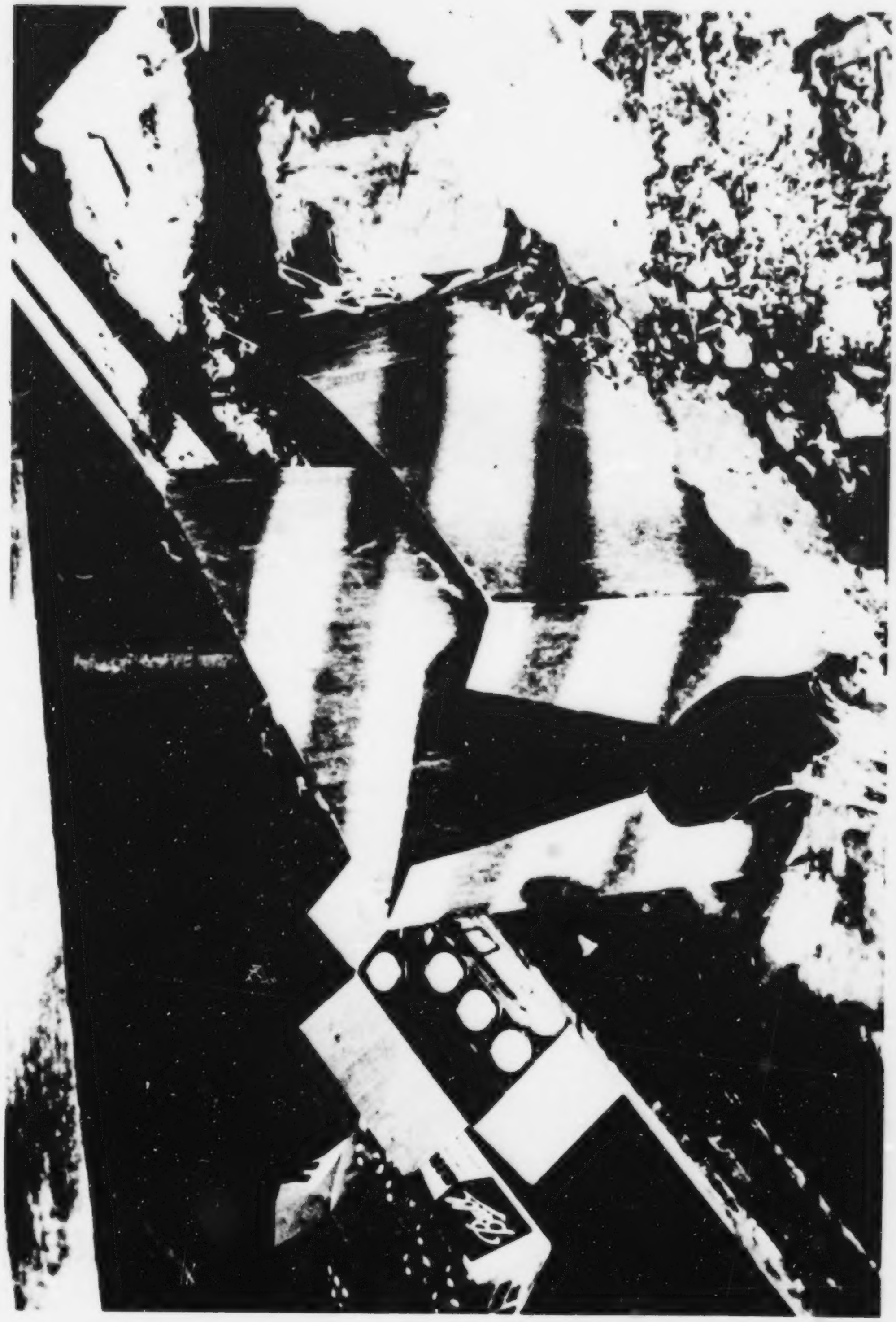


Figure 11 - No. 2 Weir with 90-Degree Notched Weir Plate in Place

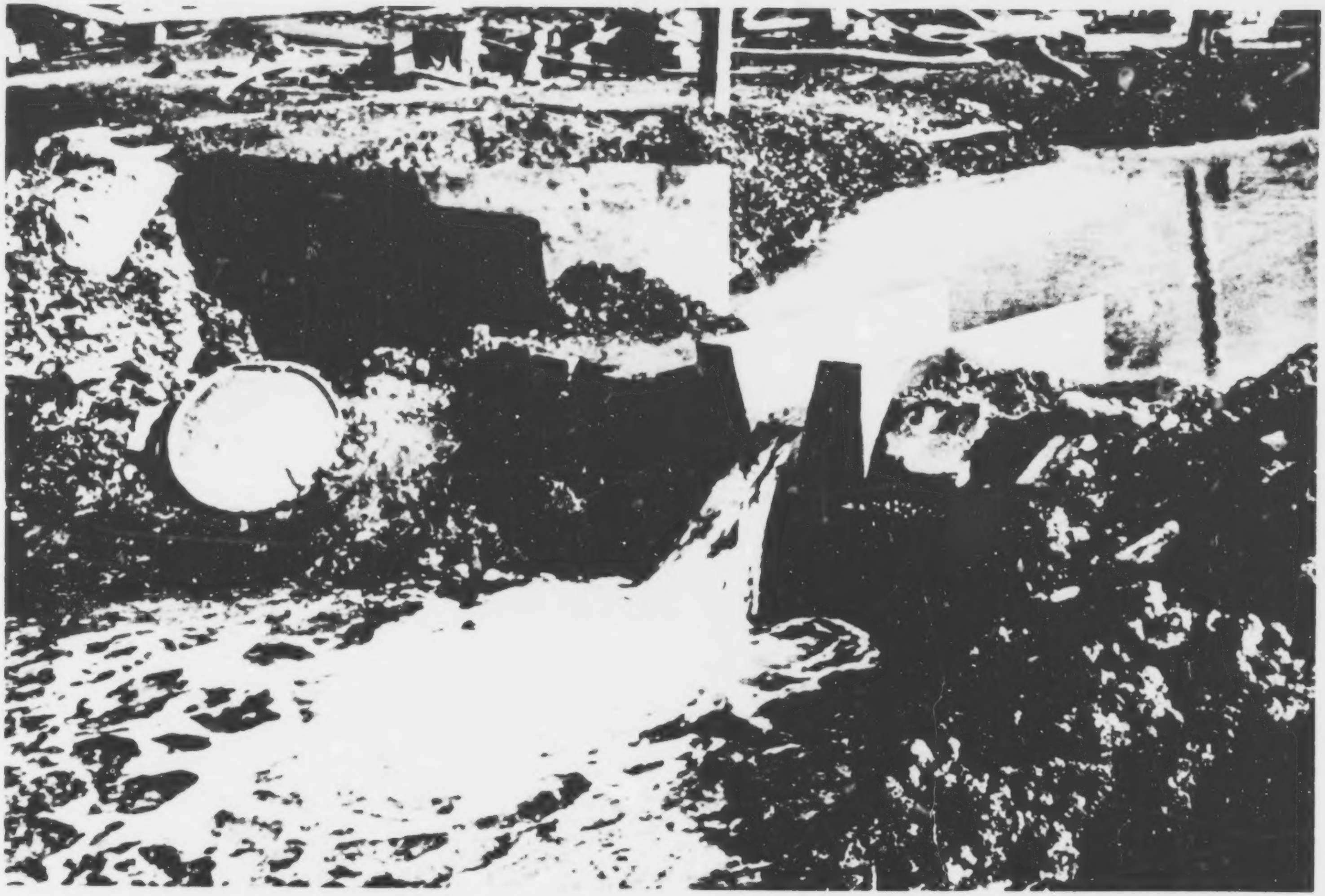


Figure 12 - Main Weir in Water Drainage Ditch Approximately 500 Feet From Mine Portal

A portable gasoline-driven Shirley Mixmeter (Model 65 AP 3x4) was set up to prepare slurries of hydrated lime and/or pulverized limestone and inject them through the 2-inch pipes to the various flooded zones behind the bulkheads. The charging tank had a capacity of 290 gallons. This machine was used to deliver the slurries through the 2-inch lines to a space behind the bulkheads (see Figure 4.) The pH meter and the slurry metering control devices on the machine were disconnected. The water used to prepare the slurries and carry them into the selected spaces behind the bulkheads was taken from the ditch just downstream of the No. 1 and No. 2 weirs by the suction line of the centrifugal pump. A portion of the slurry stream from the centrifugal pump was recycled back into the charging tank to maintain a constant level. Figure 13 shows the diagrammatic hookup of the machine. The flow rate of the recycle stream was manually controlled to keep the slurry in the charging tank thin enough to flow properly to the pump suction line - approximately 0.516 ground limestone or hydrated lime per gallon (5.67 wt%.)

The Shirley Mixmeter was run for 4 hours on October 29, 1970 to check it and other equipment, with electric power provided by a portable gasoline generator. This was later replaced by a temporary 220-volt power line that was run about 2200 feet across the south branch of Black Lick Creek to the site from Vintondale. One of the field buildings near the portal was equipped for use as a field office, storeroom and laboratory (Figure 14.) Preparations for testing were completed at the mine portal by November 3, 1970.

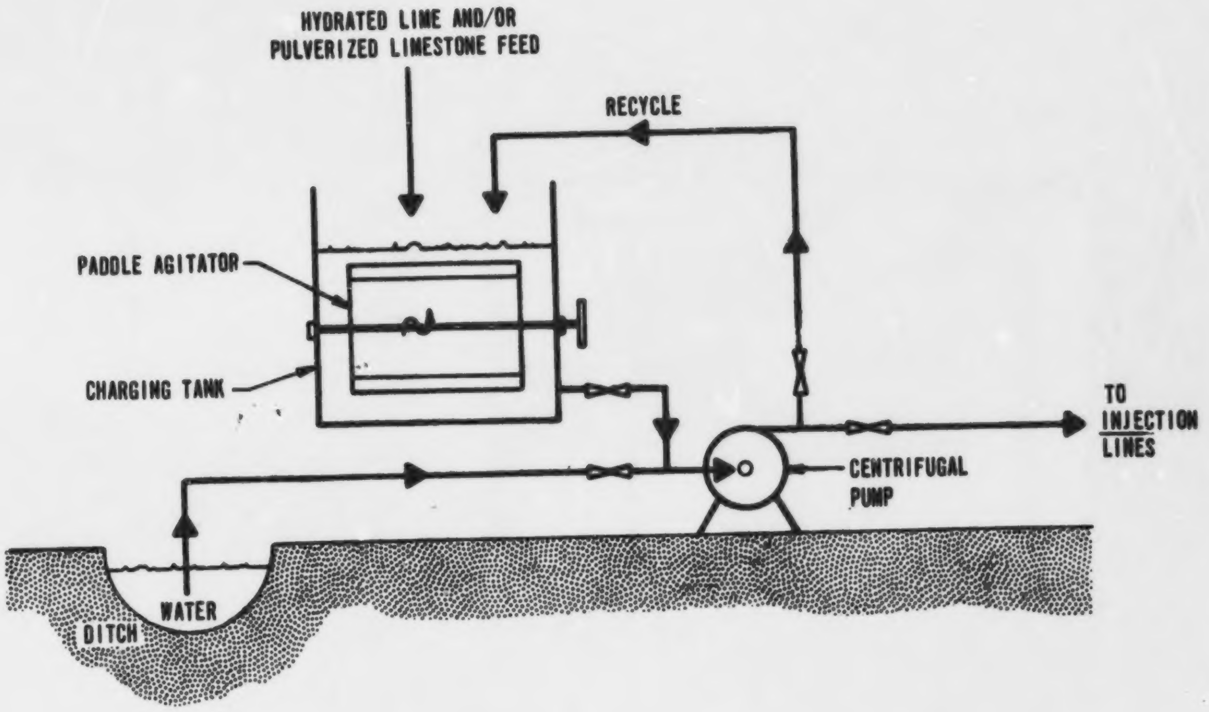

HYDRATED LIME AND/OR PULVERIZED LIMESTONE FEED
RECYCLE
PADDLE AGITATOR
CHARGING TANK
TO INJECTION LINES
CENTRIFUGAL PUMP
WATER
DITCH

Figure 13 - Shirley Mixmeter (Diagrammatic Only)

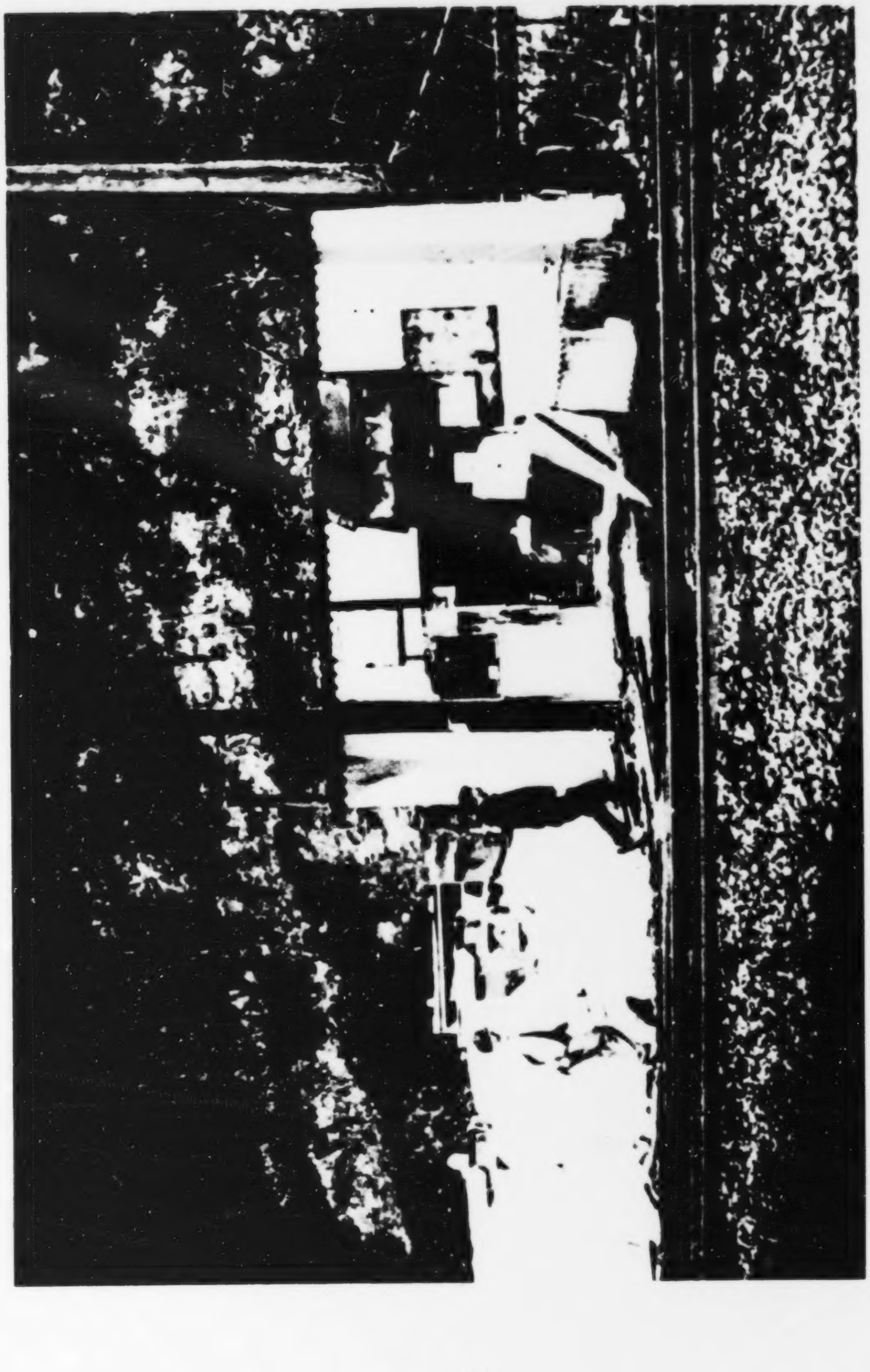


Figure 14 - View Looking North Showing Field Laboratory Building

SECTION V

TESTS AT THE MINE SITE

Operations at the mine site commenced on November 3, 1970 and continued until December 17, 1970. However, actual injection of lime slurries into the mine was not continuous during this period because of equipment breakdowns, freezing weather, rain, snow, plugged injection lines, the Thanksgiving holiday, and occasional weekend interruptions.

Tests were conducted to meet two major objectives:

> Test A: The demonstration of sealing the water flow through the rubble barrier by injecting lime slurries in the space just upstream of it.
>
> Test B: The neutralization of the acid mine water by injecting lime into the space behind a bulkhead so that the resulting precipitate of ferric and ferrous hydroxide remained in the mine, and clear, neutralized water flowed out through the 12-inch drain pipe.

These tests are described below.

TEST A, PART 1: SEAL OUTFLOW THROUGH THE RUBBLE BARRIER

A series of water samples were obtained from the mine between March 25 and April 18, 1969, and analyzed for chemical content. The results of the analyses are presented in Table 1.

Table 1 - Mine Water Content Prior to Bulkhead Construction

Date	Chemical Content (mg/1)						
	CaCO Alkalinity*						
	P	Total	Fe	Ca	Mg	Al	Mn
March 25	2120	395	1046	220	163	163	21
March 30	2188	293	1145				
April 4	2266	312	1162				
April 9	2152	295	1101	232	119	185	21
April 14	2172	188	1126				
April 18	2228	143	1161	276	113	168	21

*P = Phenolphthalein; Total = Methyl Orange

The No. 3 weir, the first installed, served to establish the flow characteristics of the total water coming out of the portal. Daily readings were taken, commencing October 22. These are presented in Table 2, together with conversions to gallons per minute. The data from Table 2 are depicted graphically in Figure 15, and show that the water outflow was slowly diminishing during the period prior to Test A. A rainstorm between October 29 and 31 washed out the No. 3 weir, and readings were not resumed until November 3.

As may be noted, rain water deposits did not appear at the portal until November 3 (about five days after the rain started), they rapidly rose to a peak of about 750 gpm, and then fell off to an average flow of about 350 gpd.

For Test A, the slurry injection schedule into the No. 1 west entry was 4 hours of hydrated lime alternating with 4 hours of pulverized limestone. A high-calcium hydrated lime (with a screen analysis of 98% through 325 mesh) and a pulverized high-calcium limestone (with a screen analysis of 82% through 200 mesh; 99.6% through 60 mesh) were used. This schedule was maintained for 40 hours, during which time a total of 6500 pounds of hydrated lime and 6050 pounds of pulverized limestone were injected.

The following 22-hour period, injection of limestone was discontinued, and 11,000 pounds of hydrated lime was injected into the space behind the rubble pile in the No. 1 west entry to raise the pH above 8; this eventually occurred.

Prior to the test, water samples were taken periodically from the No. 1 bulkhead outflow; during the test, samples were taken hourly from the No. 1 weir. These were analyzed in the field laboratory for free acid, total acid, total iron, ferrous iron, and total sulfate. Results of the analyses are summarized in Table 3.

Readings of flow and pH at the No. 1 weir were taken hourly. These data have been condensed and are summarized in Table 4.

The flow of water rapidly dropped to zero at about the 62nd hour of slurry injection, indicating that a plug had been formed in the rubble pile. A very small flow from the No. 1 weir started a few hours later at about 1 gpm and varied between zero and 1-1/2 gpm thereafter. Limestone mixed with hydrated lime was injected again at about the 65th hour and continued until the 116th hour, when the injection lines plugged. Approximately 24 hours later, one injection line was unplugged and hydrated lime was injected alone; within 9 hours, the line plugged again. When the injection lines became plugged the second time (after 149 hours), the flow from the No. 1 weir was about 1/2 gpm and the valve on the 12-inch pipe from the No. 1 bulkhead was closed. Because the valve was in a rather isolated area on the lower haulage track level of the portal, the closure was not noticed while efforts were underway to reopen the injection lines. As noted in Figure 5 (presented in Section 4), the entry between the rubble pile and the No. 1 bulkhead was filled with mine

Table 2 - Total Flow From the Portal as Recorded by the Main Weir

Date	Flow			Remarks
	Time	Inches	Gal/Min	
October 22	1600	12-1/2	325	Weir installed.
23	0800	12	300	
23	1600	12	300	
24	0800	11-1/2	270	
25	1400	11-1/4	255	
26	0800	11	245	
26	1600	10-3/4	230	
27	0800	10-1/4	200	
27	1600	10-1/4	200	
28	0800	10	195	
29		9-3/4	180	Rain started.
30		9-3/4	180	Heavy rain, 24 hours.
31		9-1/2	170	Rain diminished.
November 1				Washouts and rain damage repairs underway.
2				
3		8	120	Phase A test started.
4		11-1/2	375	
5		17-1/4	745	Flow stopped at No. 1 weir.
6	0600	8-3/4	135	
6	1200	12-1/2	335	
6	2300	14	450	Flow of 0 to 1-1/2 gpm at No. 1 weir.
7	0200	13-3/4	420	Flow of 0 to 1-1/2 gpm at No. 1 weir.
7	1800	12-3/4	350	Flow of 0 to 1-1/2 gpm at No. 1 weir.
8	0600	11-3/4	290	Flow of 0 to 1-1/2 gpm at No. 1 weir.
8	1200	12-1/2	335	Flow of 0 to 1-1/2 gpm at No. 1 weir.
9		13	370	Flow of 0 to 1-1/2 gpm at No. 1 weir.
10				Valve on No. 1 line closed.

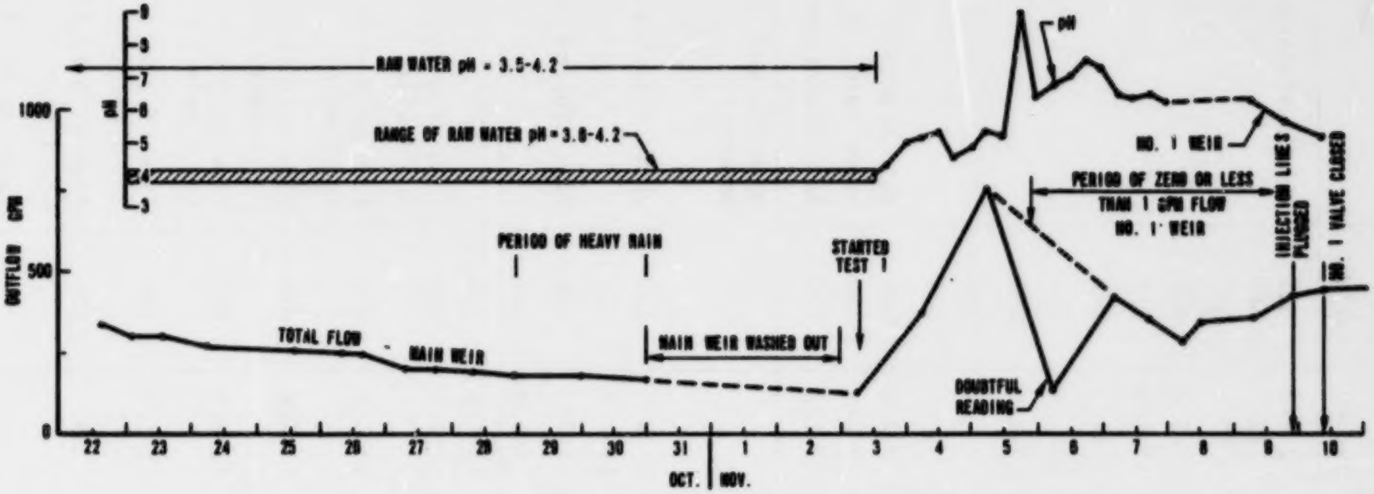


Figure 15 - Profile of Total Flow of Water From Portal at Main Weir

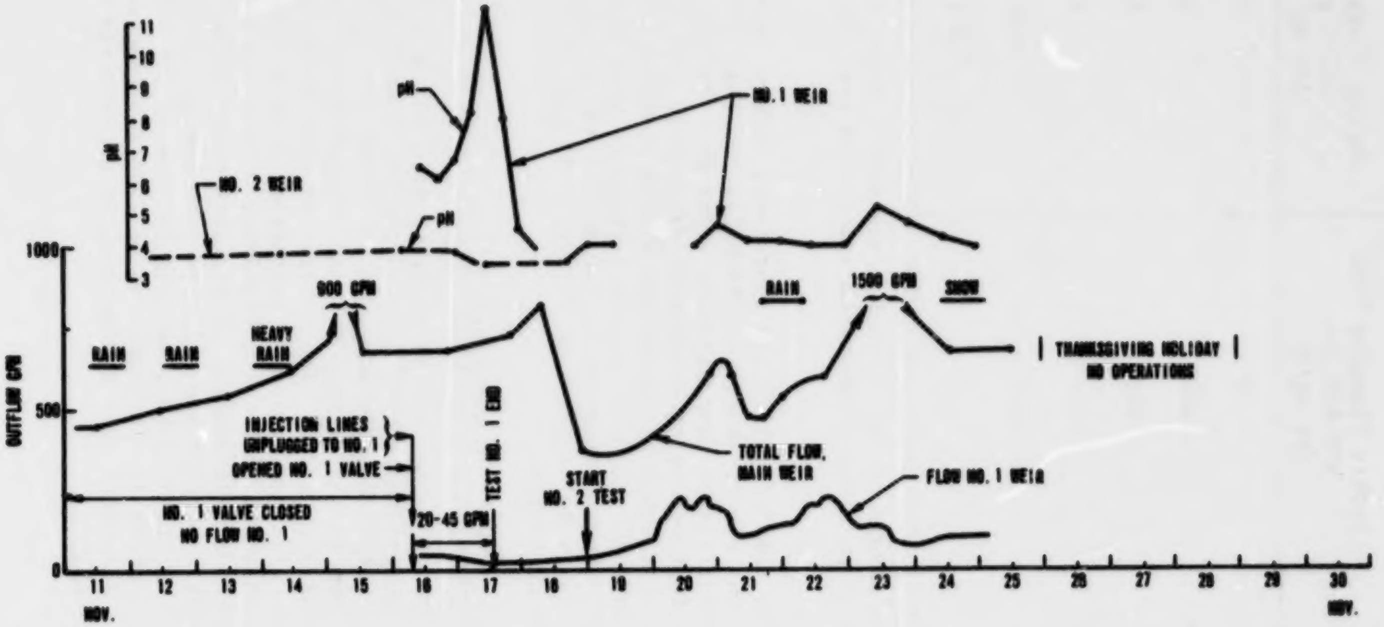


Figure 15 (Contd)

Table 3 - Analysis of Water Outflow

Component	Before Plugging Test 300-400 gpm (Av mg/l)	During Plugging Test 1/2-1 gpm (Av mg/l)
Free Acid	0	0
Total Acid	160	0
Total Fe	1400	24
Total Fe^{+2}	1000	5
Total SO_4	5000	4500
pH	5.1	8.8

water up to the invert of the 11-inch drain pipe. Thus, since the space behind the rubble pile was filled with water, the seal was under no pressure head.

In an attempt to complete all field operations before impending bad weather forced the winter shutdown, attention was then directed to the continuous neutralization demonstration (Test B). However, while the neutralization test was being conducted, efforts to unplug the injection lines into the west entry continued and proved successful. Attempts could then be made to seal off the water from the west entry. When the No. 1 valve was reopened after being closed 168 hours, the water from the west entry No. 1 bulkhead flowed at 20 to 45 gpm, indicating that the seal had deteriorated.

TEST A, PART 2 - ATTEMPT TO REESTABLISH SEAL

The equipment used for the initial plugging test was also used during the attempt to reseal the rubble pile in the No. 1 west entry. When the No. 1 valve was reopened after having been closed for 168 hours, the water issuing from the No. 1 weir box had dropped to the normal raw mine water pH level of 3.8 to 4.0. The outflow of mine water, which was 20 to 45 gpm when the valve was reopened, increased to 90 to 200+ gpm by the time the neutralization tests were completed. This led to speculation that the great reserve of acidity in the mine water in back of the plugged rubble pile barrier had diffused into the gel and redissolved the ferrous and ferric hydrates, causing failure of the initial plug. Presumably, resumption of the injection of lime slurries would reestablish the seal. To verify this assumption, an attempt was made to reestablish the seal.

Table 4 - Data Summary - Test A, Part 1: Demonstration of Plugging Water Flow Through the Rubble Barrier

Period	Duration (hr)	Addition				Water Flow (gpm)	Water pH		Total Elapsed Time (hr)	Event
		Hydrated Lime		Pulverized Limestone						
		Quantity (lb)	Rate (lb/hr)	Quantity (lb)	Rate (lb/hr)		Initial	Final		
1	40	6,500	160	6,050	151	200-500	3.9	5.4	0	Started alternate injection of hydrated lime and pulverized limestone.
2	22	11,000	500	0		150-700	4.6	6.8	40	Changed to injection of hydrated lime alone. Flow of water decreasing.
3	3	2,000		0		0		-	62	Flow of water stopped.
4	51	11,650	228	15,480	303	0-1	6.7	10.2	65	Changed to injection mixture of hydrated lime and pulverized limestone.
									102	Slight flow of water.
5	24							-	116	Injection lines plugged @ 116 hrs.

Table 4 (Contd)

Period	Duration (hr)	Addition				Water Flow (gpm)	Water pH		Total Elapsed Time (hr)	Event
		Hydrated Lime		Pulverized Limestone						
		Quantity (lb)	Rate (lb/hr)	Quantity (lb)	Rate (lb/hr)		Initial	Final		
6	9	3,000	333	0		0-1/2	-		140	Unplugged one injection line; resumed injection of hydrated lime alone.
									141	No flow of water.
7	168	0		0		0	5.4	6.3	149	Injection line plugged; closed No. 1 valve @ 149 hrs.
8	28	5,600	200	0		20-45	6.1	11.2	317	All 3 injection lines unplugged; opened No. 1 valve; resumed injection of hydrated lime alone.
9	0	-		-		-	-	-	345	Injection lines plugged; test terminated.
Total		39,750		21,530						

During the first test period, only hydrated lime was used; 39,300 pounds were injected continuously for 75 hours at a rate of 525 pounds per hour. The pH of the outflowing water rose to 10.2, but there was no significant drop in water flow. During the second test period, which lasted 22 hours, a mixture consisting of 4,400 pounds of hydrated lime and 5,440 pounds of pulverized limestone was injected with no noticeable effect on the water flow.

For the next 5 hours (the third test period), injection of hydrated lime was continued but pulverized limestone was omitted. At the same time, however, the production of sludge was increased by augmenting the mineral content of the water with waste pickle liquor containing 5 to 6% H_2SO_4 and 5 to 6% Fe^{++}, which was added to the hydrated lime slurry at a rate of approximately 1 gpm as the slurry was being injected into the mine workings. Addition of a total of 2,150 pounds of hydrated lime and 200 gallons of waste pickle liquor caused no noticeable effect on the water flow.

Throughout the next 9 hours (the fourth test period), a mixture of 1550 pounds of hydrated lime and 1280 pounds of pulverized limestone was injected without discernable effect on the outflowing water at the No. 3 weir. At this point, the Mixmeter broke down and injections could not continue until repairs were completed 29 hours later. During the repair period (Period 5), the outflowing water pH dropped to 4.7.

Injection of a mixture of hydrated lime and pulverized limestone was resumed (Period 6), but 49 hours later, after 9800 pounds of hydrated lime and 10,560 pounds of pulverized limestone had been injected, the injection system broke down again. Again the pH rose to the 11 to 12 range.

After repairs were completed 6 hours later, injection of a mixture of hydrated lime and pulverized limestone was continued again for 17 hours, during which time 3200 pounds of hydrated lime and 1680 pounds of pulverized limestone were injected - again without any effect on the water outflow.

The data from these tests are summarized in Table 5. It is evident that attempts to stop the flow of water through the rubble barrier were unsuccessful even though 60,400 pounds of hydrated lime and 18,960 pounds of pulverized limestone were injected into the entry. However, the pH of the outflowing mine water rapidly increased to the 11 to 12 range when the slurry was injected and rapidly fell off to the base mine water range when the injection stopped. After the last injection period, the water flow and pH were monitored for an additional 39 hours while arrangements were being made to shut down for the winter.

Table 5 - Data Summary - Test A, Part 2: Attempt to Reestablish the Seal in the West Entry No. 1

Period	Duration (hr)	Addition				Water Flow (gpm)	Water pH		Total Elapsed Time (hr)	Event
		Hydrated Lime		Pulverized Limestone			Initial	Final		
		Quantity (lb)	Rate (lb/hr)	Quantity (lb)	Rate (lb/hr)					
1	75	39,300	525	0		20-90	3.8	10.2	0	Started injection of hydrated lime alone.
2	22	4,400	200	5,440	245	20-90	12.1	12.3	75	Changed to injection of mixture of hydrated lime and pulverized limestone.
3	5	2,150	430	0		65-90	12.1	12.3	97	Started injection of hydrated lime and waste pickle liquor.
4	9	1,550	175	1,280	142	65-115	12.3	11.9	102	Changed to injection of mixture of hydrated lime and pulverized limestone.
5	29	0		0		25-115	12.0	4.7	111	Equipment Breakdown.

Table 5 (Contd)

Period	Duration (hr)	Addition				Water Flow (gpm)	Water pH		Total Elapsed Time (hr)	Event
		Hydrated Lime		Pulverized Limestone			Initial	Final		
		Quantity (lb)	Rate (lb/hr)	Quantity (lb)	Rate (lb/hr)					
6	49	9,800	200	10,560	216	25-55	5.0	11.7	140	Resumed injection of mixture.
7	6	0		0		35-45	10.5	8.5	189	Equipment breakdown.
8	17	3,200	188	1,680	210	35-80	8.5	11.6	195	Resumed injection of mixture.
9	39	0		0		55-114	5.3	4.1	212	Stopped injection of mixture.
10	0	-		-		-	-	-	251	Test terminated.
Total		60,400		18,960						

TEST B, PART 1: CONTINUOUS NEUTRALIZATION

Test B, Part 1, the continuous neutralization of the outflowing water, was conducted behind the No. 2 bulkhead (see Figure 4). The water from this area of the mine flowed out of the No. 2 weir and was relatively isolated from the lime injection behind the No. 1 bulkhead. Flow from behind the No. 2 bulkhead was controlled by the No. 2 valve at the downstream end of the 12-inch pipeline just before it entered the No. 2 weir.

For the purposes of this test, the No. 2 valve was partially closed to reduce the water flow to approximately 150 gpm, and, once adjusted, was not changed for the duration of the test. However, the flow varied from 130 to 200 gpm, presumably because of changes in the head in the mine.

For this test, a slurry containing 0.5 pound of hydrated lime per gallon was prepared using two Shirley Mixmeters. After 200 gallons of water were pumped into the charging tank of the first Mixmeter, the mixing arm was started and 100 pounds of hydrated lime were added. The charge was mixed until a uniform slurry was formed. A similar charge was prepared in the charging tank of the second Mixmeter. To provide a continuous supply of hydrated lime slurry during the test, as each charging tank was emptied, a new charge was prepared. The Mixmeters were used only as slurry mixers and the batches were transferred to a 55-gallon open-end drum which served as a feed tank for four small paddle pumps. Each pump was connected to one of the six 2-inch injection lines that passed through the No. 2 bulkhead into the mine. The four injection lines used were Nos. 2 and 3 which terminated 65 and 50 feet into the north entry and Nos. 5 and 6 which terminated 105 and 90 feet into the west entry beyond the bulkheads. Each of these pumps had a capacity of 2 gpm of slurry; since they were operated together, a total of 8 gpm of slurry was injected when the tests were made.

After 39 hours, use of the paddle pumps was discontinued because the rotors were worn out, terminating the first period of the slurry injections. Operations were stopped until replacement pumps could be obtained. Both before and after the test the mine water had a pH of 3.8 to 4.5, which indicated no lasting effect of the lime injection.

Theoretically, a dosage rate of 4.0 pounds of hydrated lime per minute should raise a pH of 3.5 to 11.1. However, this did not occur; the actual mine water readings at the No. 2 weir ranged from 3.6 to 4.6 during the 39-hour period that the hydrated lime slurry was injected.

The Period 2 test was conducted with a gasoline-driven pump, which permitted the injection of the lime slurry at a higher rate than the Period 1 test; i.e., 20 gpm. The outflow of mine water was the same, and the pH, ranging from 4.4 to 4.5 during the 10-hour period between the tests, was essentially the same. Theoretically, the lime injection rate in this test was sufficient to raise a pH of 3.5 to 12. Again, however (as shown in Table 6) the outflowing water failed to respond to the treatment and its pH ranged from 4.4 to 4.8 during the 26 hours of testing.

Table 6 - Continuous Neutralization Test Behind No. 2 Bulkhead

Test Period	Duration (hr)	Slurry Injection Rate (gpm)	Hydrated Lime Addition		Flow of Mine Water		Ratio of Lime to Mine Water (gm/liter)	pH at No. 2 Weir	
			lb/min	Total Pounds	gpm	liters/min		Theoretical	Actual
1	39	8	4.0	9,360	130-200	492-757	2.40-3.69	11.1	3.6-4.6
-	10	0	-	-	130-200	492-757	-	-	4.4-4.5
2	26	20	10.0	15,600	130-200	492-757	6.00-9.23	12.0	4.4-4.8

TEST B, PART 2: DYE INJECTIONS

Failure of injection of the hydrated lime into the mine workings behind the No. 2 bulkhead to increase the pH of the outflow at the No. 2 weir raised the question of where the outflow was coming from. Therefore, a series of dye solution injections were made to determine the flow pattern of the water draining from the 12-inch No. 2 drain line. Both the north entry and the No. 2 west entry were tested in this manner. The dye solution was prepared by thoroughly mixing 2 ounces of methylene blue in 50 gallons of mine water. The injections were made using the 20-gpm pump, and took 2 minutes to complete.

North Entry

During the first dye test, the dye solution was injected through the No. 1 injection line into the North Entry at a point 80 feet from the No. 2 bulkhead (see Figure 4). The control valve in the 12-inch drain line was opened completely, which gave a 900-gpm outflow of mine water. In this test, the dye appeared at the discharge of the No. 2 drain line 30 minutes after it was injected. The outflow was allowed to continue for approximately 2 hours to purge the dye from the north entry so that the dye testing could be repeated with a reduced flow.

In the next part of this test, the control valve was partially closed to restrict the discharge flow to 150 gpm, and a second injection of dye solution was made under the same pumping conditions. This time the dye solution did not appear at the discharge point after 4 hours, which was long eough to drain a volume of water from a mine one-third greater than that necessary to show the dye at the higher rate of outflow.

No. 2 West Engry

For the second dye test, the dye solution was injected through injection line No. 4 into the No. 2 west entry at a point 120 feet from the No. 2 bulkhead (see Figure 4).

As in the first dye test, the valve controlling the 12-inch drain line was left completely open and discharged mine water at a rate of 900 gpm. This time the dye appeared at the discharge 60 minutes after it was injected into the mine entries.

With the valve again partially closed to restrict the discharge flow to 150 gpm, a second injection of dye solution was made. Observation of the outflow for approximately 8 hours revealed no dye at the discharge outlet. As before, the volume of water drained from the mine at the low outflow rate exceeded the volume that showed the dye at the high outflow rate by one-third. Results of the dye tests are summarized in Table 7.

Table 7 - Dye Injection Tests

Test Condition		Results
Injection Point	No. 2 Valve Position	
No. 2 Line (180 ft in north entry)	Fully open (Approx 900 gpm)	Dye appeared within 30 minutes
	Partially open (Approx 150 gpm)	No dye appeared after 4 hours
No. 4 Line (120 ft in No. 2 west entry)	Fully open (Approx 900 gpm)	Dye appeared within 60 minutes
	Partially open (Approx 150 gpm)	No dye appeared after 8 hours

The dye tests indicated that the flow pattern of the water adjacent to the ends of the injection lines in the north entry and the No. 2 west entry changes when the outflow from behind the No. 2 bulkhead is changed. Obviously, when the valve is wide open, the flow at the end of the injection line is sufficient to carry the dye into the 12-inch pipe at the No. 2 bulkhead. When the valve was partly closed, the outflow was insufficient to bring the dye to the inlet of the 12-inch pipe. Presumably, this same effect was occurring when the slurry was being injected. Thus, any effect of acid water neutralization by the hydrated lime would not be observed at the weir box for the flow rate of 150 gpm. Injection of the slurry at flow rates substantially greater than 20 gpm, to be compatible with the 900-gpm outflow rate, was not possible with the existing equipment.

FOLLOWUP INSPECTION OF MINESTIE, SPRING 1971

A field inspection of the minesite was made on May 3, 1971, after the relatively mild winter. The weirs were still in place and no subsidence or othe/damage was observed at the portal. Weir and pH measurements made at the site are summarized in Table 8.

Table 8 - Followup Weir Data

Time (hrs)	No. 1 Weir		No. 2 Weir		Main Weir	
	Flow (gpm)	pH	Flow (gpm)	pH	Flow (gpm)	pH
800	15	4.2	454	3.8	560	3.9
830	16	4.3	530	3.7	545	3.9
900	15	4.1	545	3.7	560	3.9
930	15	4.3	545	3.8	560	3.8
1000	15	4.2	545	3.9	560	3.8
1030	16	4.2	545	3.9	560	3.9
1100	16	4.2	545	3.8	560	3.8
1130	16	4.2	545	3.8	560	3.8
1200	16	4.2	545	3.8	560	3.8

Elevations were measured on the bottoms of the 12-inch discharge pipes, and showed that the No. 2 pipe is 0.62 foot lower than the No. 1 pipe. The valves on both pipes were wide open and No. 2 pipe was blowing full. The higher pH at the No. 1 weir indicates that the lime slurry injected into the No. 1 west entry is still causing some neutralizing effect.

The No. 2 and main weirs were badly corroded by the acid water.

SECTION VI

TEST RESULTS

SEALING

After hydrated lime and ground limestone had been injected into the acid mine water behind the rubble pile for 65 hours (Table 4), the flow through the emplaced rubble pile was reduced from approximately 500 gpm to zero. Thus, the initial sealing was successful.

Although the flow had been reduced to zero when the seal was first accomplished, some water began to seep at the rate of about 1-1/2 gpm, as observed at the No. 1 weir during the test period, until the 149th hour, at which time the valve was closed. Continued injections of lime and/or limestone had no effect in reducing these seepages to zero.

An attempt was made to reestablish the seal when the No. 2 valve was reopened, but it failed. Even adding waste sulfate pickle liquor to augment the minerals in the water and produce a higher volume of precipitate failed.

As the pH of acid mine water is raised by the reaction of neutralizing agents with the acid water, dissolved ferrous and ferric ions precipitate as a sludge consisting of hydroxides or hydrated oxides. The calcium from the lime forms calcium sulfate, most probably gypsum, which is crystalline and only slightly soluble. The form and characteristics of this sludge can vary extensively, depending on such variants as water constituents, neutralizing agents, and the rate of addition of neutralizing agents. While the sludge varies from a light, fluffy floc to a dense particulate precipitate, it is always in a nonfilterable form that would blind a filtering medium. Its nonfilterability is the basis for using the sludge to seal drainage openings, using the water flow to carry the sludge into the voids to plug them.

However, for the precipitated sludge to be effective, the size of the voids or channels that the sludge is to seal must not exceed some unknown maximum. It is certain that the precipitate, when relatively freshly formed, did indeed stop the flow of water through the channels of the rubble pile. Flows of 1/2 to 1 gpm are not regarded as significant indications of seal failure; hence, it was during the time that the No. 1 valve was closed (after 149 hours) that the seal failed, and flows of 20 to 45 gpm could be observed when the valve was reopened. Two factors may have contributed to this: (1) the well-known shrinkage of gels as they age may have loosened the plugs, and (2) diffusion of acid mine water into the gelatinous plugging material may have caused re-solution of the iron hydrate gel. It is entirely possible that the neutralization of the acid mine water at the face of the

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rubble barrier was badly impaired by the stratification of the lime slurry precipitate and its flow downslope into the mine depths. This could have occurred when the slurry fell from the ends of the injecting pipes to the floor of the entry. Since the water at the face of the rubble barriers was stagnant, once the seal was established there was no flowing force to carry or hold the injected slurry and precipitates into the channels and maintain the seals. When the seal failed later and water flows upward of 100 gpm set in, the efforts to reestablish the seal could have failed because the sandbag seal at the top of the barrier had failed and the resulting channels were too large for the gel to close. The sandbags had been in position for approximately a year and protected only the last 18 to 24 inches of the 25-foot crown of the rubble pile that had settled a few inches beneath the entry roof.

During the tests to reestablish the seal, the outflowing mine water was highly alkaline and slightly murky because of blue-green iron hydrates. This led to the hypothesis that one or more of the injection lines had been ruptured between the No. 1 bulkhead and the rubble pile, and that slurry was issuing in that zone. The rupture of the injection line could have been caused by the efforts to clear the pluggages and possibly from corrosion by the acid mine water during the 13 months or so between their placement behind the No. 1 bulkhead and the commencement of the tests. However, it is postulated that the bulk of the gel rapidly sank to the floor of the entry and was unable to act as a sealing agent near the roof at the top of the rubble barrier, even though approximately 40 tons of material had been pumped into the mine.

The laboratory tests revealed that the sludge does, in fact, stop the flow of water through a porous sand barrier. Seals were formed within minutes, remained watertight for weeks, and withstood calculated hydrostatic heads up to 200 feet. Laboratory tests were performed using 2-inch tubes to simulate a coal mine adit that measured 4.5 by 14 feet at Driscoll No. 4. Under laboratory conditions, such problems as the settling of particles in the porous barrier and movement of surrounding rock do not affect the long-term stability of the seal. In the field, however, these problems could become serious. The breakdown of the seal in the field was disappointing, especially since the cause of the breakdown could not be determined. While many explanations could be postulated, the sole cause cannot be determined with any degree of certainty. A combination of factors was probably to blame.

It is possible that, in trying to reopen the plugged injection lines, the compressed air that was forced into the injection lines stirred up the exposed layer of sludge that formed part of the seal. If this was the cause of the breakdown, then a fast development of the seal is undesirable because the sludge does not have the opportunity to penetrate very deeply into the rubble pile and can easily be disturbed.

It would also indicate that a lower dosage level would be desirable so as to form the sludge at a slower rate. The increased water flow for a longer period of time would then carry the sludge farther into the rubble pile. Although it would take longer to develop a seal, the seal might be more durable.

Another possibility is that the initial composition of the ferrous hydroxide sludge gradually converts to a hydrated ferric oxide, which has a higher density than the ferrous hydroxide. This would result in shrinkage cracks similar to the mud cracks that develop as a lake bottom dries up. If this was the cause of the breakdown, the need for the development of the seal at a slower rate is again indicated. The conversion of lightweight, green, fluffy floc to a reddish granular form characteristic of precipitating ferric ion, as hydrated ferric oxide, was observed in the laboratory. With the seal forming at a slower rate, more time would be available for the oxidation of the ferrous hydroxide to the hydrated ferric oxide, and additional sludge could fill the cracks as they develop. The seal, once achieved, would not be subject to the crack formation from subsequent shrinkage. This shrinkage phenomenon was observed in the sludge settling in the bed of the drainage ditch immediately upstream of the main weir, but downstream of the screen across the ditch. Although the sludge was always submerged and never subjected to drying, cracks developed in the sludge that was deposited in the relatively quiescent pond. Figure 16 shows one of the quiet spots where the cracks were observed.

It is also possible that during the injection of limestone some of the limestone does not react with the acid water, perhaps due to poor dispersion in forming a slurry, and is carried with sludge into the rubble pile to react subsequently with acid water. Carbon dioxide would be liberated and, if formed in a large pocket, could suddenly erupt, breaking the seal.

CONTINUOUS NEUTRALIZATION

During the first 39-hour period of the continuous neutralization trials, the dosage level of the lime addition should have resulted in a rise in pH to 11.1. However, the pH never rose above 4.6. During the next 10-hour period, when no lime was added, the pH did not drop significantly. During the last 26-hour period, the dosage level of lime addition should have resulted in a pH rise to 12. However, during this period the pH did not rise above 4.8.

The dye tests showed that when the No. 1 valve was only partially open, and the outflow of mine water was low, the flow from the end of the injection pipe to the inlet of the 12-inch drain pipe was essentially nonexistent. Conversely, with the valve fully open, the high rate of outflow from the drain pipe created a rapid flow from the injection points to the drain pipe inlet. This shows that when the lime slurry was injected, there was essentially no flow toward the drain pipe; hence, there was no increase in pH, as anticipated.

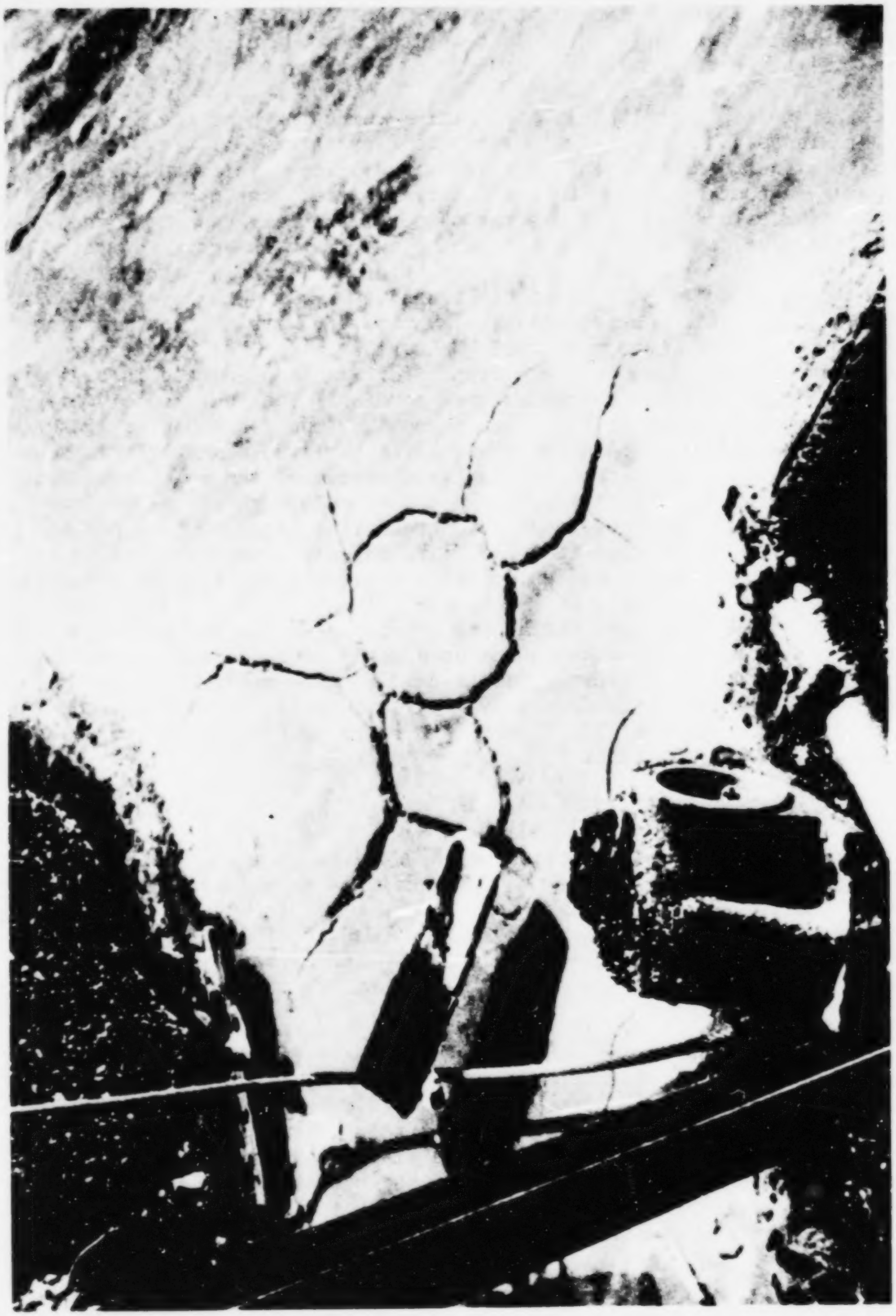

Figure 16 - Sludge Settled in a Stagnant Area of Drainage Ditch

Calculations indicate that the 24,960 pounds of hydrated lime added during the 65 hours of slurry injection were sufficient to react with gradually rose to 11, then 12 during the lime injection and remained liter of Fe^{++} and 700 milligrams per liter of Fe^{+++}. The volume of the entries behind the No. 2 bulkhead to 10 feet beyond the ends of the injection lines is estimated to be on the order of 90,000 gallons. Thus, about 3.4 times more hydrated lime was added than was necessary to neutralize the iron content of this mine water. The flow rate from the No. 2 lines was 130 to 200 gpm; hence, 585,000 to 900,000 gallons. Thus, water outflowed during the 75-hour test period (including the 10 hours between Test 1 and Test 2 when no slurry was injected.) Consequently, there were between 8.2 to 12.7 theoretical water changes in the entries during the test period, which would be a change every 5.9 to 9.1 hours. Since the dye tests did not show any flow to the drain from the injection point at this level of outflow, there must have been a significant flow away from the injection points into the depths of the mine.

During some rough bench tests in the field laboratory, it was also observed that the floc formed by the reaction of the lime slurry and the mine water rapidly settled to the bottom of the vessel in large clumps or curds. This probably took place at the end of the injection pipes located at the roof of the entries. The inlet to the 12-inch drain pipe is also at the roof where it comes through the No. 2 bulkhead. Any stratification of the lime precipitates at the bottom of the entry, back to the inlet of the drain pipe, would have approximately 2 to 3 feet before its level reaches the inlet to the 12-inch drain pipe. Thus, the flow away from the drain inlet and the rapid settling of the lime-mine water floc to the entry floors combined to migrate the lime slurry reaction products away from the drain. This would explain the negative result of the continuous neutralization tests.

The probability that this method of treatment can be successfully applied is indicated by the results obtained while attempting to reestablish the seal in the rubble pile. The pH of the discharging water, which was 3 to 4 prior to resumption of the lime injection, gradually rose to 11, then 12 during the lime injection and remained at 12 during the lime and limestone injection. When the injection was stopped, the pH dropped back into the 3 or 4 range. When the injection of a lime and limestone slurry was resumed the pH again rose to approximately 11, then gradually dropped back to approximately 4 after the injection was stopped for the last time in preparation for shutting down the test site.

Thus, while a seal was not reestablished, continuous neutralization of the acid mine water (without the iron oxidation step) was taking place and, presumably, the sludge being formed was settling back into the mine.

SECTION VII

ACKNOWLEDGEMENT

The support and assistance of the Department of Mines and Mineral Industries of the Commonwealth of Pennsylvania, through the loan of a Shirley Mixmeter for use during the field test program, is acknowledged with sincere thanks.

This report was prepared by the Parsons-Jurden Division, The Ralph M. Parsons Company, 617 West Seventh Street, Los Angeles, California 90017 for the Commonwealth of Pennsylvania, Department of Environmental Resources, Harrisburg, Pennsylvania.

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SECTION VIII

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SECTION IX

ALPPENDIX: LABORATORY INVESTIGATIONS

SUMMARY

The laboratory investigations were conducted to assist in a study of underground precipitation in acid mine water so as to select materials and formulate a program for the field demonstration phase at the test mine. The program had three objectives: filling mine voids, plugging drainage openings, and continuous neutralization of mine effluent. Individual studies of each concept were made. Within budgetary limits, these studies were made in sufficient depth to determine their applicability or, if this could not be done, to determine whether additional work would be recommended.

It was necessay to develop several basic test procedures for use in the various evaluations. Bulking ratios resulting from the addition of various materials were determined, and plugging capabilities of precipitates obtained with various materials were evaluated. Effects of size and composition of feed materials, of air agitation, and of static head on plugging properties were studies. A wide range of acid mine waters was tested to determine the effects of various pH ratios on precipitation of metal ions and to determine the composition of acid mine water which could be treated effectively. Other studies included: gelling of acid mine water with synthetic gelling agents, coating of mine surfaces by precipitates formed in situ, augmentation of mineral content of acid mine water by addition of waste pickle liquor, and continuous neutralization of acid mine water.

The use of fly ash in connection with coal mine pollution abatement was investigated separately by G. & W.H. Corson, Inc., and results made available for use in this study are included in this report.

Except for the fly ash investigation, all of the laboratory work described in this volume was performed by personnel of G. & W.H. Corson, Inc. at their laboratory facilities in Plymouth Meeting, Pa., under the supervision of the cognizant Project Engineer.

The individual tests and results are summarized below.

EFFECT OF pH ON PRECIPITATION OF METAL IONS IN ACID MINE WATER

Titration of individual aqueous solutions of Fe^{++}, Fe^{+++}, and Al^{+++} as sulfate salts with sodium hydroxide solutions indicate that: Fe^{+++} precipitates in the pH range of 1.5 to 3.5; Fe^{++} precipitates in the pH range of 3 to 8.5; and Al^{+++} precipitates in the pH range of 2.5 to 5. Precipitated Al^{+++} redissolves at pH of 10 or over.

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BULKING RATIOS OBTAINED DURING PRECIPITATION

A simple test was used to determine bulking ratios of various candidate materials. Bulking ratio is defined as the volume of precipitate formed in acid mine water by a weighed quantity of material divided by the volume occupied by the same weight of the additive material in deionized water. High-calcium and dolomitic limestones and lime products were evaluated. The highest bulking ratios were achieved using dolomitic monohydrated lime. In general, both the dolomitic monohydrated and dolomitic dihydrated limes gave higher bulking ratios than did high-calcium hydrated limes; pulverized limestones yielded lower bulking ratios than did hydrated limes; and high-calcium limestone gave higher bulking ratios than did dolomitic limestone.

Bulking ratio depends partly on the type of material, and partly on the dosage (quantity of additive relative to amount of mine water, i.e., grams additive per liter of mine water). As the dosage is increased the bulking ratio at first remains constant (or may apparently increase) up to a point, and then decreases, showing that after all the mineral content as precipitated, further additions of reactants increase the total volume of precipitate but only at a bulking ratio of one, thus lowering the overall bulking ratio.

Nine limestones and five hydrated limes locally available near Vintondale were evaluated to form a basis for selection of specific limestones and hydrated limes to be used during the field demonstration phase. The limestone yielding the highest bulking ratio was Gold Bond #10 pulverized limestone. The hydrated limes yielding the highest bulking ratio were New Enterprise Hydrated Lime and Chemical Hydrated Lime (Standard Lime).

PLUGGING CHARACTERISTICS OF PRECIPITATES FORMED UNDERGROUND

Three test procedures were considered for evaluating plugging by precipitates. The simplest procedure, the static plugging test, is most expedient for screening candidate materials. The vertical dynamic plugging test is somewhat more complicated, but more closely approximates mine conditions where constant flow of mine water exists. The horizontal dynamic plugging test substitutes a horizontal tube for the vertical tube that represents the main adit. Except for scale, this is more realistic in approximating actual mine conditions, but the additional time and apparatus were not considered justified for this refinement. Therefore, the vertical dynamic plugging test was selected. Results of plugging tests made with all three methods indicate that, although bulky, precipitates formed underground in acid mine water are capable of plugging the voids in a porous obstruction through which the water must pass.

STUDIES TO OPTIMIZE SIZING OF FEED MATERIALS AND COMPOSITIONS VERSUS PRECIPITATE BULKING

Three variables in the composition of the slurry injected into the mine adit were of interest in their possible effect on the neutralization and precipitation in the mine water: the particle size of the additive material, the solids content of the slurry, and the quality of the water in the slurry. The studies performed show that: (1) specification of particle size is important for pulverized limestone but not for hydrated lime, providing a good quality, correctly calcined and slaked material is specified; (2) slurry concentration is not critical if a good dispersion is obtained; and (3) the quality of the water used to make up the slurry is not critical.

EFFECT OF AIR AGITATION ON BULKING RATIOS AND PLUGGING CHARACTERISTICS

The purpose of introducing air into acid mine water is to convert ferrous iron to the ferric state, since ferric iron precipitates at a lower pH than does ferrous iron. However, the conversion proceeds very slowly at the lower pHs (approximately pH 3) and somewhat more rapidly at slightly higher pHs (pH 5 or 6). Therefore, introducing air at the lower pH would not be as effective as at the higher pH. Also, ferrous iron precipitates are much bulkier than ferric iron precipitates (which tend to be more particulate) so that even though more iron would be precipitated, the total volume of precipitate might be lower than if precipitated at the higher pH. Therefore, air agitation appears to be either useless or even detrimental in creating as high a bulking ratio as possible.

On the other hand, air agitation might be beneficial from a pH standpoint because a precipitate having a somewhat particulate structure is presumably more favorable to plugging. However, the results of the tests in this area are not conclusive.

EFFECT OF STATIC HEAD ON PLUGGING CHARACTERISTICS

Tests on a "fresh" seal formed by the precipitate formed in the mine water flowing into and plugging the voids in the drainage channel indicate that the seal can withstand a pressure of 100 feet of water backed up behind it with no appreciable increase in permeability. It is assumed that additional precipitate formed as the injection of the slurry continues, together with "aging" of the seal, will result in a seal which can withstand even higher pressures. (Gels are known to have aging characteristics, generally observed as shrinking and the appearance of liquid drops on the surfaces. Presumably they gain in strength with age.)

COMPOSITION OF ACID MINE WATER WHICH CAN BE TREATED EFFECTIVELY

Within the wide range of acid mine waters tested, all could be successfully treated to result in high bulking precipitates with good plugging properties. Where high acidity was present, a large amount of additive slurry was required to raise the pH sufficiently to precipitate all of the mineral content in the water. At higher acidities, however, the precipitates do not bulk as much as at lower acidities.

GELLING OF ACID MINE WATER WITH SYNTHETIC GELLING AGENTS

Cellulose gum is capable of gelling water containing heavy metal ions since the heavy metal ions react with the cellulose gum to cross-link and result in gel structures of varying degrees of rigidity, depending on concentrates of reactants. Under favorable conditions, the reaction proceeds slowly enough to allow the cellulose gum to be mixed with the acid mine water and to be pumped back into the mine adit before the reaction proceeds far enough to produce the gel. In this way the gel structure is produced underground in the mine adit. Good dispersion of the cellulose gum in the acid mine water is essential.

COATING OF MINE SURFACES BY PRECIPITATES FORMED UNDERGROUND

Precipitates formed underground in the acid mine water do not appear to have any value for selectively coating and sealing pyrites contained in the coal.

AUGMENTATION OF MINERAL CONTENT BY ADDITION OF WASTE PICKLE LIQUOR

Augmentation of mineral content of acid mine water, when necessary because of reduced mine water flow, can be done with waste pickle liquor (sulfate) from the steel industry. Addition of such waste pickle liquor raises the acidity as well as the mineral content, thereby requiring additional slurry.

CONTINUOUS NEUTRALIZATION OF ACID MINE WATER

The laboratory tests indicate the feasibility of continuous neutralization of acid mine drainage by injection of the slurry into the adit, and allowing the precipitate to flow back down the adit to lower portions of the mine. However, because of the difficulty of correlating laboratory work with field conditions, it appeared to be more productive to plan a field demonstration as the next step.

USE OF FLY ASH

The usefulness of fly ash depends on its composition and its ability to augment deficient constituents in the mine water. Fly ash is capable of entering into a reaction to produce ettringite ($6CaO \cdot Al_2O_3 \cdot 3SO_4 \cdot 33H_2O$), with accompanying expansive forces. Ettringite contains calcium, aluminum, and sulfate ions. Replacement of part of the calcium with magnesium appears to be beneficial. Replacement of some of the aluminum with iron is possible, thus allowing the utilization of iron in acid mine water in the formation of the ettringite structure. When all the ingredients are present, either within the fly ash itself or through augmentation, good results are obtained, both from the standpoint of filling mine voids and plugging effluent drainage flows.

Fly ash of the proper composition is capable of hardening when placed in contact with acid mine water. However, while some slight expansion does take place, the bulking ratio is insignificant. The resultant solid structure is very hard, making it useful even though the bulking ratio is very low.

When the fly ash is added to flowing acid mine water to seal an effluent drainage channel, the fly ash (together with whatever augmentation materails may be required) tends to flow into and plug the interstices of a rubble barrier present in the drainage channel. From this standpoint the use of the proper fly ash, or properly augmented fly ash, gives excellent results.

Since fly ash of the proper composition was not readily available near the demonstration site, augmentation would be required which would be costly at this site. Therefore, fly ash should be evaluated at a later date at a more suitable mine site.

TEST 1

EFFECT OF pH ON PRECIPITATION OF METAL IONS PRESENT IN ACID MINE WATER

The metal ions present in acid mine waters consist mainly of iron (ferrous, ferric, or a mixture of both) and aluminum. Therefore, a knowledge of the effect of pH on the precipitation of these ions is of basic interest in the underground precipitation concept for abatement of pollution due to acid mine water.

In individual tests, aqueous solutions of Fe^{++}, Fe^{+++}, and Al^{+++} were prepared by dissolving the sulfate salt of each metal in deionized water. These individual solutions were then titrated, using a sodium hydroxide solution, to determine the pH at which each hydroxide precipitate first appears, and the pH at which precipitation is complete. In the case of Al^{+++}, titration was continued to the point at which the precipitate starts to redissolve. Sodium hydroxide was used for these titrations because the sodium sulfate formed during the neutralization, being water soluble, would not interfere with the visual observation of the resultant precipitation.

LABORATORY PROCEDURE

Ferrous Iron

For the ferrous iron test, 0.5 g of $FeSO_4$ was dissolved in a minimum quantity (9.17 ml) of 0.3042N H_2SO_4, and diluted to 100 ml with distilled water. The H_2SO_4 is required to lower the pH to below the precipitation point. This solution was then titrated with 0.5046N NaOH. The pH at which precipitation started and at which precipitation was complete was determined.

Ferric Iron

To test ferric iron, 0.5 g of $Fe_2(SO_4)_3$ was dissolved in a minimum quantity (26.88 ml) of 0.3042N H_2SO_4, and diluted to 100 ml with distilled water. The H_2SO_4 was required to lower the pH to below the precipitation point. This solution was then titrated with 0.5046N NaOH. The pH at which precipitation started and at which precipitation was complete was determined.

Aluminum

For testing aluminum, 0.5 g of $Al_2(SO_4)_3$ was dissolved in a minimum quantity (8.42 ml) of 0.3042N H_2SO_4, and diluted to 100 ml with distilled water. The H_2SO_4 was required to lower the pH to below the precipitation

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point. This solution was then titrated with 0.5046N NaOH. The pH at which precipitation started and at which precipitation was complete was determined. In addition, the titration was continued until the precipitate began to redissolve.

RESULTS

Results of these tests indicate that ferric iron precipitates in the pH range of 1.5 to 3.5, ferrous iron in the pH range of 3 to 8.5, and aluminum in the pH range of 2.5 to 5. Precipitated aluminum redissolves at a pH of 10 and over. The experimental data are shown in Table 1-1 and Figure 1-1.

Table 1-1 - Continuous Titration of Fe^{++}, Fe^{+++}, and Al^{+++} With NaOH

Time (min)	NaOH (ml)	Fe^{++} pH	Fe^{+++} pH	Al^{+++} pH
0	0	1.39	1.32	1.80
0.1	1.08	1.40	1.38	1.80
0.2	2.16	1.47	1.38	1.89
0.3	3.24	1.51	1.38	2.02
0.4	4.32	1.60	1.38	2.24
0.5	5.42	1.65	1.40	2.59 *
0.6	6.48	1.70	1.41	3.45
0.7	7.56	1.80	1.50 *	3.77
0.8	8.67	1.90	1.52	3.92
0.9	9.72	2.02	1.60	4.02
1.0	10.80	2.26	1.67	4.13
1.1	11.88	2.36	1.76	4.26
1.2	12.96	2.65	1.81	4.71 **
1.3	14.04	3.15 *	1.95	8.00
1.4	15.12	4.06	2.03	9.20
1.5	16.20	5.78	2.18	> 10 ***
1.6	17.28	6.60	2.37	-
1.7	18.36	7.23	2.58	-
1.8	19.44	7.58	2.74	-
1.9	20.52	7.80	3.03	-
2.0	21.60	8.10 **	3.32 **	-
2.1	22.68	9.96	5.98	-
2.2	23.76	-	7.71	-
2.3	24.84	-	9.74	-

* First precipitate.
** Precipitation complete.
*** Precipitate redissolves.

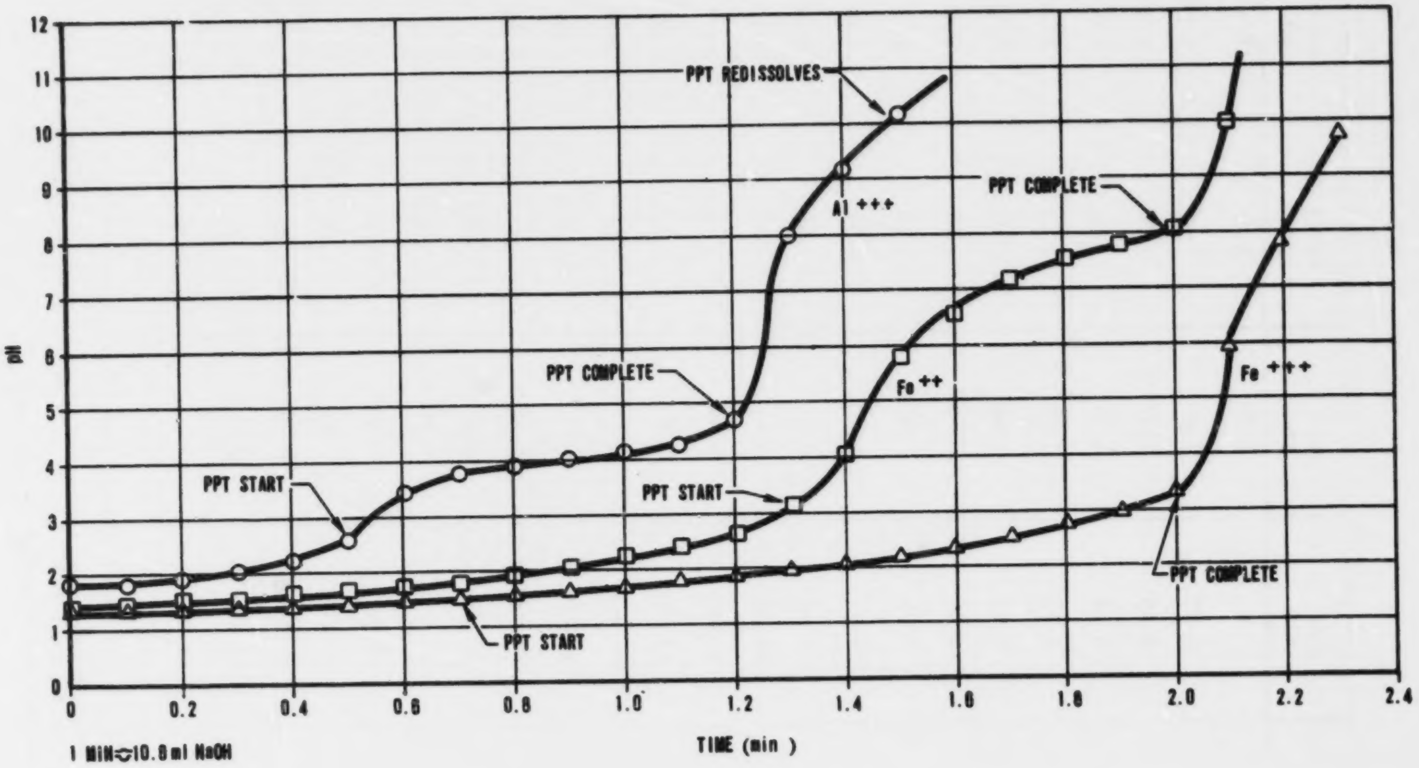

Figure 1-1 - Titration of Fe^{++}, Fe^{+++} and Al^{+++} with NaOH

TEST 2

BULKING RATIOS

One of the main objectives in considering the precipitation concept for abatement of pollution from acid mine water is to achieve as high a bulking ratio as practical during the neutralization. The bulking ratio, in this context, is defined as the ratio of the volume of precipitate formed when a given quantity of reactant is added to mine water, to the volume occupied by the same quantity of reactant when added to distilled water. Therefore, the bulking ratio gives an indication of the economic leverage gained by the use of reactants rather than unreactive additives such as sand, gravel, and concrete (which would have bulking ratios of one).

LABORATORY PROCEDURE

Synthetic mine water was prepared in accordance with a recommendation by Dr. Harold L. Lovell of The Pennsylvania State University. This consisted of deionized water to which was added 300 mg/l of Fe^{++} (as $FeSO_4$) and 75 mg/l of Al^{+++} [as $Al_2 (SO_4)_3$], with the pH adjusted to 3.0 by addition of H_2SO_4. There is no typical acid mine water, but this synthetic water included a moderate concentration of the two predominant metal ions found in acid mine waters. The pH of 3 was an average figure most likely to be encountered at an actual mine site.

A slurry was prepared by adding a given quantity of additive to 50 ml of distilled water. This slurry was then added to a liter of synthetic mine water contained in a graduated cylinder. The cylinder was allowed to stand undisturbed for 18 hours, and the volume of the precipitate (which usually settled to the bottom of the graduate) was noted. The pH of the water was also noted to determine what degree of neutralization had been achieved.

In conducting bulking tests following this test method, it must be recognized that: (1) reading the volume of precipitate is subject to a large experimental error; and (2) the volume of precipitate produced varies considerably when tests are repeated under supposedly similar conditions. Difficulty in reading the precipitate volume is due to the nature of the apparatus; the variation in the volume of precipitate is due to the complexity of the hydrated iron oxides produced. Because of these two inherent sources of variation, differences in volume of precipitate must be evaluated on the basis of order-of-magnitude differences rather than on an absolute difference basis.

EVALUATION OF TYPICAL LIMESTONES AND LIMES

The prime candidates for neutralizing materials are the limestones and lime products, which have high neutralization values, are readily available, and low in cost.

Limestones fall into two basic types: high-calcium limestone and dolomitic limestone. High-calcium limestone consists of $CaCO3$, plus impurities such as SiO_2, and has a minimum of 98% $CaCo_3$. Dolomitic limestone consists of $CaCO_3$ and $MgCO_3$, plus impurities such as SiO_2. High-calcium limestone occurs throughout the Commonwealth of Pennsylvania. However, dolomitic limestone is found mainly in Eastern Pennsylvania, thus limiting its use to the eastern portions of the state, unless its performance is superior enough to offset the cost of transportation.

The hydrated limes fall into three basic types: high-calcium hydrated lime, monohydrated dolomitic lime, and dihydrated dolomitic lime. High-calcium hydrated lime conists of $Ca(OH)_2$, and is made by hydrating calcined high-calcium quickline. It will have 92% to 95% $Ca(OH)_2$. Monohydrated dolomitic lime consists of $Ca(OH)2$, MgO, and is made by hydrating calcined dolomitic limestone under atmospheric pressure conditions. Dihydrated dolomitic lime consists of $Ca(OH)_2$, $Mg(OH)_2$, and is made by hydrating calcined dolomitic limestone at pressures above atmospheric.

Nine materials typical of this group of products were selected for the initial evaluation. The characteristics of these materials are shown in Table 2-1.

The highest bulking ratios were achieved using monohydrated dolomitic lime. In general, the hydrated dolomitic limes gave higher bulking ratios than did high-calcium hydrated lime; pulverized limestones yielded lower bulking ratios than hydrated limes; and high-calcium limestone gave higher bulking ratios than dolomitic limestone.

From the standpoint of neutralization, the high-calcium hydrated lime yielded a higher pH than the hydrated dolomitic lime; hydrated lime yielded a higher pH than the pulverized limestone; and dolomitic limestone yielded a higher pH than the high-calcium limestone.

A study of the bulking ratios achieved (Table 2-2) shows that as the additive level (g/l of mine water) is increased, the bulking ratio at first remains constant (or may apparently increase - "apparently" because at very low levels of addition it is difficult to read the volume of precipitate accurately) up to a point, then decreases. This is explained by the fact that after all the mineral content has precipitated (and assuming no redissolving of minerals), further

Table 2-1 - Characteristics of Typical Limestone and Dolomitic Lime Products

Type	Product	Screen Analysis	Specific Gravity	Loose Bulk Density (lb/ft^3)	Volume Occupied By 100 gm in H_2O (ml)	Approximate Price (fob Quarry) ($/ton)
High-Calcium	Pulverized Limestone	95% thru 200 mesh	2.72	100 - 120	78	5.00
	Quicklime	100% thru 10 mesh	3.34 - 3.40	50 - 60	*	15.50
	Hydrated Lime	90% thru 325 mesh	2.30	35 - 45	268	16.00
Dolomitic	Pulverized Dolomite	95% thru 200 mesh	2.84 - 2.88	100 - 200	72	5.00
	Selectively Calcined Dolomite	100% thru 10 mesh	2.90 - 3.00	75 - 80	78	14.00
	Quicklime (Soft Burned)	100% thru 10 mesh	3.40 - 3.45	45 - 50	*	15.50
	Monohydrated Dolomitic Lime	90-95% thru 325 mesh	2.60 - 2.65	35 - 45	150	14.50
	Milled Dihydrated Dolomitic Lime	90-95% thru 325 mesh	2.40 - 2.50	35 - 40	224	19.00
	Unmilled Dihydrated Dolomitic Lime	85-90% thru 325 mesh	2.40 - 2.50	35 - 40	206	18.50

*Assumed to be same as for corresponding hydrated lime.

Table 2-2 - Comparison of Volume of Precipitate and Bulking Ratio Achieved
(Produced by Different Types of Limestones and Hydrated Limes
When Added as a Water Slurry to Synthetic Acid Mine Water - SAMW)

Grams of Reactant per Liter of SAMW	High-Calcium Limestone						Dolomitic Limestone											
	Pulverized Stone		Quicklime		Hydrated Lime		Pulverized Stone		Selectively Calcined Stone		Soft Burned Quicklime		Monohydrated Lime		Milled Dihydrated Dolomitic Lime		Unmilled Dihydrated Dolomitic Lime	
	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio	PPT Vol (ml)	Bulking Ratio
0.2	*	--	25	46.6	50	93.3	*	--	*	--	7	23.3	45	150.0	10	22.3	10	26.2
0.5	**	--	25	18.7	90	67.2	**	--	5	12.8	65	86.7	80	106.7	35	31.2	25	24.3
1.0	10	12.8	50	18.7	85	31.7	**	--	5	6.4	100	66.7	115	76.7	70	31.2	65	31.6
1.5	15	12.8	70	17.4	75	18.6	5	4.6	5	4.3	110	48.8	120	43.6	75	22.3	70	22.7
2.0	20	12.8	100	18.7	70	13.1	5	3.5	10	6.4	100	33.3	115	38.3	80	17.6	75	18.2
3.0	20	8.6	75	9.3	75	9.3	5	2.3	15	6.4	80	17.8	100	22.2	75	11.1	70	11.3
4.0	20	6.4	75	7.0	75	7.0	5	1.7	25	8.0	80	16.7	80	13.3	60	6.7	55	6.7
5.0	20	5.1	60	4.5	80	6.0	5	1.6	25	6.4	95	12.7	95	12.7	70	6.2	50	4.6

*Much less than 5 ml.
**Less than 5 ml.

additions of reactants increase the total volume of the "precipitate," but only at a bulking ratio of 1, since there is no further chemical reaction. Therefore, the additional volume lowers the overall bulking ratio.

A study of the pHs achieved (Table 2-3) shows that pulverized stone can raise the pH of the water only to 4.5 to 5.0, while the hydrated limes can raise it higher. No leveling off of the pH was noted within the addition level of 5 g/l of hydrated lime used in these tests. However, the pHs achieved, being 8 or over, were high enough to precipitate all the iron present (ferrous as well as ferric).

EVALUATION OF LOCALLY AVAILABLE MATERIALS

A survey of specific commercially available products from sources located near the demonstration mine site revealed no dolomite deposits within a reasonable distance. Therefore, only high-calcium limestone and hydrated lime made from high-calcium limestone were considered for use in the demonstration phase. Fourteen lime products (nine limestones and five hydrated limes) from five local producers, were selected as candidate materials. Characteristics of these 14 products are shown in Tables 2-4 and 2-5.

Results of the tests with the commercial lime products are shown in Tables 2-6 and 2-7, which list volume of precipitate and bulking ratio, and the pH of solution after 18 hours, respectively.

The highest bulking ratio achieved by the limestones was 30 for the addition of 1 gram of Gold Bond #10 pulverized limestone to 1 liter of acid mine water. The pH of the solution was raised to 4.3. The Bell Mine #90 pulverized limestone raised the solution pH to 4.35 (for the same addition level); however, the bulking ratio was only 10.

The highest bulking ratio achieved by the hydrated limes was 67 for the addition of 1/2 gram of New Enterprise Hydrated Lime to 1 liter of acid mine water. However, the pH of the solution was raised to only 4.1, indicating much mineral content still remaining in the solution. Since the limes are capable of precipitating all the mineral content (even redissolving some such as aluminum at higher pH0, a more meaningful criterion for rating effectiveness if the weight of material required to raise the solution pH to the range of 10 to 11. On this basis, the most effective lime was Standard's Chemical Hydrated Lime, which required 2 g/l to reach a pH of 11; next was National's Chemical Hydrated Lime #26, which required 3 g/l; next was Bell Mine Chemical Hydrated Lime, which required 5 g/l; next was New Enterprise's Hydrated Lime, which at 5 g/l raised the pH to 10.8. Nittany Hydrate performed more like a limestone than a lime. At the 2 g/l addition level, the bulking ratio varied from 6.1 to

Table 2-3 - Comparison of pH Resulting From Addition of Different Types of Limestones and Hydrated Lime (Injected as a Water Slurry to Synthetic Acid Mine Water)

Grams of Reactant per Liter of SAMW	High-Calcium Limestone			Dolomitic Limestone					
	Pulverized Stone	Quick-lime	Hydrated Lime	Pulverized Stone	Selectively Calcined Stone	Soft Burned Quick-lime	Mono-hydrated Lime	Milled Dihydrated Lime	Unmilled Dihydrated Lime
0.2	4.5	5	4.5	5.0	4.5	4.5	4.5	5.0	4.5
0.5	4.5	5	5.0	5.0	4.5	4.5	4.5	5.0	4.5
1.0	4.5	5	5.5	5.0	4.5	4.5	5.0	5.0	5.0
1.5	4.5	-	5.5	5.0	4.5	5.0	5.5	5.0	5.0
2.0	4.5	6	6.0	5.0	4.5	6.0	5.5	5.0	5.5
3.0	4.5	9	-	5.0	5.0	7.0	8.5	5.0	7.0
4.0	4.5	-	8.5	5.0	5.0	8.5	9.0	8.0	8.5
5.0	4.5	10	11.0	5.0	5.0	9.5	9.5	8.0	9.0

Table 2-4 - Characteristics of Locally Available Pulverized Limestones

Trade Name	Supplier	Screen Analysis	Loose Bulk Density (lb/cu ft)	Delivered Price, Bulk (June 1969) ($/ton)
Code 55 Limestone	Standard Lime & Refr. Co.	100% -3/8 in.	110-115	4.65
Dry CAL-AG	Standard Lime & Refr. Co.	70-90% -20	80-90	5.15
Gold Bond Screenings #20	National Gypsum Co.	100% -1/8 in.	90-100	4.75
Gold Bond #10 PLS	National Gypsum Co.	81.5% -200 99.6% -60	55-70 (loose) 95-100 (packed)	9.60
Wet Kiln Sludge	Warner Company	87% -325 100% -4	39 (dry basis)	11.00 (dry basis)
Bell Mine #90 PLS	Warner Company	60% -325 100% -30	60 (loose) 95 (packed)	9.95
Pennsylvania No. 1 Stone	New Enterprise Stone & Lime Co.	100% -1/4 in.	NA	4.65
Asphalt Filler	New Enterprise Stone & Lime Co.	85% -200 100% -20	NA	7.00
Agricultural Limestone	Sproul Lime & Stone Co.	60% -100 100% -20	105	6.50

Table 2-5 - Characteristics of Locally Available Hydrated Limes

Trade Name	Supplier	Screen Analysis	Loose Bulk Density (lb/cu ft)	Delivered Price, Bulk (June 1969) ($/ton)
Washington Chemical Hydrate	Standard Lime & Refr. Co.	98% -325	25	21.10
Chemical Hydrated Lime #26	National Gypsum Co.	95.3% -325 99.8% -100	20 (loose) 43 (packed)	21.40
Bell Mine Chemical Hydrated Lime	Warner Company	99% -325 100% -30	25	22.20
Nittany Hydrate	Warner Company	24% -100 100% -4	42	12.95
Hydrated Lime	New Enterprise Stone & Lime Co.	95% -325 100% -200	NA	25.50

Table 2-6 - Comparison of Volume of Precipitate and Bulking Ratio Achieved (Produced by Specific Grades of Limestone and Hydrated Limes from Nearby When Added as a Water Slurry to Synthetic Acid Mine Water)

Grams of Reactant per Liter of SAMW	Pulverized Limestone																			
	Typical Limestone		Code 55 Limestone		Dry CAL-AG		Gold Bond Screenings #20		Gold Bond #10 PLS		Wet Kiln Sludge		Bell Mine #90 PLS		Pennsylvania No. 1 Stone		Asphalt Filler		Agricultural Limestone	
	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR
0.5	*	-	**	-	**	-	***	-	20	40.0	**	-	15	15.0	**	-	**	-	25	12.5
1.0	10	12.8	**	-	15	3.8	***	-	30	30.0	**	-	20	10.0	**	-	10	10.0	30	15.0
1.5	15	12.8	**	-	25	4.2	***	-	25	16.7	**	-	20	6.7	**	-	20	13.3	35	11.7
2.0	20	12.8	**	-	30	3.8	***	-	25	12.5	**	-	20	5.0	**	-	25	12.5	25	6.3
3.0	20	8.6	10	1.7	40	3.3	***	-	30	10.0	**	-	25	4.2	10	3.3	30	10.0	30	5.0
4.0	20	6.4	15	1.9	45	2.8	***	-	35	8.8	**	-	20	2.5	15	3.8	35	8.8	30	3.9
5.0	20	5.1	20	2.0	50	2.5	***	-	35	7.0	10	1.3	20	2.0	20	4.0	25	5.0	30	3.0

Grams of Reactant per Liter of SAMW	Hydrated Lime											
	Typical Lime		Wash. Chemical Hydrate		Chemical Hydrated Lime, #26		Bell Mine Chemical Hydrated Lime		Nittany Hydrate		New Enterprise Hydrated Lime	
	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR	PPT Vol (ml)	BR
0.5	90	67.2	90	51.5	90	36.0	65	29.0	10	6.7	100	67.0
1.0	85	31.7	120	34.4	90	18.0	70	15.6	15	5.0	105	35.0
1.5	75	18.6	80	15.3	85	11.3	60	8.9	20	4.5	75	16.7
2.0	70	13.1	60	8.6	65	6.5	55	6.1	30	5.0	55	9.2
3.0	75	9.3	70	6.7	60	4.0	50	3.7	35	3.9	55	6.1
4.0	75	7.0	60	4.3	60	3.0	50	2.8	40	3.3	50	4.2
5.0	80	6.0	70	4.0	70	2.8	65	2.9	45	3.0	60	4.0

*Less than 5.
**Less than 10.
***No reaction, additive settled to bottom as lumps.

BR = Bulking Ratio

Table 2-7 - Comparison of pH Resulting from Addition of Specific Grades of Limestones and Hydrated Limes from Nearby Quarries (Injected as a Water Slurry to Synthetic Acid Mine Water)

	Pulverized Limestone										Hydrated Lime					
Grams of Reactant per Liter of SAMW	Typical Limestone	Code 55 Limestone	Dry CAL-AG	Gold Bond Screening #20	↓ Gold Bond #10 PLS	Wet Kiln Sludge	Bell Mine #90 PLS	Pennsylvania #1 Stone	Asphalt Filler	Agricultural Limestone	Typical Lime	↓ Washington Chemical Hydrate	Chemical Hydrated Lime, #26	Bell Mine Chemical Hydrated Lime	Nittany Hydrate	New Enterprise Hydrated Lime
0.5	4.5	3.3	3.65	3.1	3.9	3.3	3.9	3.6	3.95	3.9	5.0	4.1	4.4	3.7	3.2	4.1
1.0	4.5	3.4	3.8	3.15	4.3	3.5	4.35	3.7	4.1	4.1	5.5	5.5	5.9	4.6	3.4	8.9
1.5	4.5	3.8	3.7	3.25	4.7	3.6	5.1	3.75	4.2	5.0	5.5	10.6	10.6	4.7	3.5	10.3
2.0	4.5	3.8	4.0	3.35	4.8	3.7	5.0	3.8	4.3	5.1	6.0	11.0	10.8	10.3	3.7	10.5
3.0	4.5	3.8	4.1	3.5	4.8	3.7	5.1	3.9	4.5	5.0	---	11.1	11.0	10.4	3.8	10.5
4.0	4.5	3.9	4.1	3.8	4.8	3.7	5.1	3.9	4.6	4.9	8.5	11.1	11.2	10.8	3.8	10.7
5.0	4.5	4.1	4.3	3.85	4.8	3.7	5.0	3.9	5.2	4.9	11.0	11.5	11.7	11.0	3.8	10.8

9.2 (excluding the Nittany Hydrate). However, when comparing at a given addition level, the volume of precipitate is more important than the bulking ratio because the actual volume is of greatest practical interest. In terms of volume of precipitate, the volumes at the 2 g/l addition level varied from 55 to 65 ml (excluding the Nittany Hydrate).

SUMMARY

The initial investigation indicated that hydrated limes were more effective than pulverized limestones. Hydrated dolomitic limes appeared to be more effective than high-calcium limes; however, high-calcium limestone appeared to be more effective than dolomitic limestone.

Because dolomitic limestone was not readily available at the demonstration mine site, only high-calcium limestones and hydrated limes were included in the evaluation of specific grades available locally. In this evaluation, it appears that where limestone is used, the limestone should be Gold Bond #10 Pulverized Limestone, as supplied by the National Gypsum Co. Where hydrated lime is used, it should be the Washington Chemical Hydrate, as supplied by Standard Lime & Refractories Co.

TEST 3

PLUGGING CHARACTERISTICS OF THE PRECIPITATES

The second main objective in connection with the underground precipitation concept for abatement of pollution from acid mine water is to form precipitates that will seek out and plug drainage outlets. From this standpoint, bulking ratio is not as important as plugging ability; however, high bulking precipitates having superior plugging ability are the most desirable.

LABORATORY PROCEDURE

Since there was no experimental procedure available to evaluate the plugging characteristics of the precipitates, a suitable test method had to be developed. The apparatus first used in this investigation consisted essentially of a vertically positioned glass tube, 2 inches in diameter and 4 feet long, with the lower end inserted in a Buchner filter, with a rubber sleeve to form a watertight seal. A layer of coarse sand (-10+14) was placed in the tube, on top of the perforated filter plate, and a layer of fine sand (-60+100) was placed over the coarse sand. A short length of rubber tubing and hose clamp were placed on the funnel outlet, and 2000 ml of synthetic mine water (see Test 2) was placed in the tube. A slurry of the reactant was then added to the mine water, and the resulting mixture allowed to stand undisturbed for 18 hours. After that time, the hose clamp was removed and the time required to draw off 100 ml of the liquid from the bottom of the funnel was determined. A similar draw-off of 100 ml was made when the liquid head had been reduced to 17 inches. This test is identified in this program as the static plugging test because the slurry addition is done as a single addition to a static pool of water.

To more closely approximate actual field conditions, the static head condition was replaced by one in which water flowed at a constant rate before the addition of the slurry, also at a constant rate. The apparatus was as above, except that the funnel effluent was unrestricted after passing through the sand bed, and a continuous feed of synthetic mine water was supplied to the top of the tube. The incoming feed rate was adjusted to 545 ml per minute to yield one tube volume change in 5 minutes. When approximately 1000 ml of water was contained in the glass tube, a constant feed of water slurry of the reactant was started. The funnel discharge rate was constantly measured, and the time required to reduce the discharge rate to one drop per second was noted; then both water feed and slurry feed were stopped. Eighteen hours after the feeds were stopped, the tube was refilled to the original height, and the time between drops was measured. The tube was refilled daily to the original

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height and the time between drops noted. This test is identified in this program as the vertical dynamic plugging test because the water and slurry are added at a continuous constant rate and because the glass tube is positioned vertically.

The test was then further modified to simulate a horizontal mine adit with a vertical borehole placed behind a rubble pile at the effluent end. The tube was placed in a "horizontal" position (1% slope down to the effluent end), and the Buchner funnel was replaced with a piece of wire retaining screen. Layers of coarse and fine sands were placed behind the wire screen, and the mine water feed was started. The flow was adjusted to 700 ml/min to simulate the linear velocity of a mine flow of approximately 450 bpm in a 7 by 7 foot mine adit (1 foot per second). When the water feed had been stabilized, the water slurry feed, adjusted to a preselected rate, was started. The slurry was added through a vertical side tube situated just behind the sand layers. Discharge rate through the wire screen was measured; when the flow rate reduced sufficiently, the time between drops was measured. This test is identified in this program as the horizontal dynamic plugging test.

RESULTS

Results of tests using the static plugging test are shown in Table 3-1. High-calcium hydrated lime, monohydrated dolomitic lime, and pulverized high-calcium limestone were evaluated at various addition levels. All decreased the flow rate of water through the sand layer at the bottom end of the tube to a great degree. The high-calcium hydrated lime was more effective than the monohydrated dolomitic lime; both limes were more effective than the pulverized limestone.

Results of the tests using the vertical dynamic plugging test are shown in Table 3-2. Again, all three materials were able to decrease the flow rate of water through the sand layer to a great extent--in some cases, rather quickly; in others, after a short time. Some tests developed channeling through the sand and had to be discontinued. In these tests the monohydrated dolomitic lime appeared to be more effective than the high-calcium hydrated lime. However, the most effective reduction in flow rate was obtained with a massive dose rate using high-calcium limestone. In this test, 23 grams of limestone were added per liter of mine water. Time to reduce flow (from 545 ml/min) to one drop per second could not be measured within the time limit of the working day. At the end of the first day, the rate was reduced to 1.4 seconds between drops. At the end of 7 days, this rate had been reduced to 17 seconds between drops. At the end of 14 days, the rate was 43 seconds between drops.

The horizontal dynamic plugging test was developed to investigate the possibility that the precipitates formed in the mine water would not flow horizontally to plug a vertically positioned sand bed. These tests were performed using high-calcium hydrated lime and pulverized high-calcium limestone. Results, shown in Table 3-3, are typical of a number of test

Table 3-1 - Decrease in Flow Rate Through Sand Due to Precipitation in Acid Mine Water (Using Static Plugging Test)

Lime Product	Reactant Addition (g/1)	Time For Flow of 100 ml (min)	
		At 44-Inch Head	At 17-Inch Head
High-Calcium Hydrated Lime	0.5	7.5	41.0
	1.0	20.2	70.0
	1.5	31.5	205.0
	2.5	31.5	150.0
Monohydrated Dolomitic Lime	0.5	10.0	21.0
	1.0	NA	24.5
	1.5	14.0	57.0
	2.0	20.0	67.0
	2.5	14.0	67.0
	3.5	16.5	58.5
Pulverized High-Calcium Limestone	0.5	0.4	1.3
	1.0	0.8	2.7
	1.5	NA	2.2
	2.5	2.0	10.5
	3.5	5.0	14.5
Water Only	0	0.05	0.09

Table 3-2 - Decrease in Flow Rate Through Sand Due to Precipitation in Acid Mine Water (AMW)
(Using Vertical Dynamic Plugging Test)

Inflow (545 ml/min)							Outflow						
Additive	Run No.	Total Volume of AMW (ml)	Total Volume of Additive Slurry (l)	Concentration of Additive in Slurry (%)	Total Wt of Additive Added to AMW (gh)	Wt of Additive to Volume of AMW (g/l)	Time to Reduce Flow to 1 drop/sec (min)	pH to Effluent at 18 hr	Time Between Drops (sec)				
									After 1 Day	After 3 Days	After 5 Days	After 7 Days	After 14 Days
High-Calcium Hydrated Lime	80	10	0.5	0.4	2	0.2	9	6.0	1.5	0.5	*	*	*
	66	10	0.5	1.0	5	0.5	19	6.0	0.5	0.5	0.8	0.9	1.5
	69	10	1.0	0.5	5	0.5	36	8.0	0.0	1.5	2.2	-	3.1
	75	10	0.5	2.0	10	1.0	6	11.5	3.0	2.3	-	1.4	2.9
	83	10	0.5	3.0	15	1.5	10	12.5	5.0	5.0	6.0	9.5	**
	84	10	0.5	4.0	20	2.0	4	12.5	0.0	1.5	2.6	3.9	**
	86	10	0.5	5.0	25	2.5	3.5	12.5	0.8	3.0	3.5	3.2	2.0
Monohydrated Dolomitic Lime	79	10	0.5	0.4	2	0.2	14	5.5	4.5	4.0	-	2.5	0.0
	71	6	1.0	0.5	5	0.84	36	11.5	1.2	-	4.5	3.5	3.3
	68	6	1.0	1.0	10	1.67	***	12.5	1.2	-	7.0	7.5	4.0
	85	10	0.5	4.0	20	2.0	4	12.5	3.8	5.0	9.0	11.0	14.5
	76	4	0.5	2.0	10	2.5	10	12.5	3.8	-	5.0	7.0	11.0
	85A	10	0.5	5.0	25	2.5	4	12.5	3.5	5.5	7.2	8.0	10.0
	82	3	0.5	3.0	15	5.0	7.5	12.5	6.0	8.0	9.0	8.3	7.0
Pulverized High-Calcium Limestone	67	10	0.5	1.0	5	0.5	18.0	4.0	1.0	1.8	1.8	1.7	1.4
	70	10	1.0	0.5	5	0.5	8.0	4.0	1.1	1.1	1.2	1.5	1.0
	72	10	1.0	2.0	20	2.0	5.0	5.0	0.5	1.8	-	1.8	2.0
	73	10	1.0	4.0	40	4.0	***	5.0	1.3	2.8	5.0	8.0	15.0
	74	3	0.5	13.8	69	23.0	***	5.5	1.4	3.2	6.0	17.0	43.0

* Test discontinued after 4 days
** Test discontinued after 7 days
*** Time went beyond working day

Table 3-3 - Decrease in Flow Rate Through Sand Due to Precipitation in Acid Mine Water (Using Horizontal Plugging Test)

Test Run	A	B	C
Treatment	Slurry of high-calcium hydrated lime	Slurry of high-calcium hydrated lime and pulverized high-calcium limestone	Slurry of pulverized high-calcium limestone followed calcium hydrated lime
Initial Flow Rate (ml/min)	700	700	700
Effluent Flow Rate - Sand in Place (ml/min)	400	450	430
Effluent Flow Rate - After Treatment (drops/sec)	1	2	2.2
Effluent Flow Rate - After 1 Week (drops/sec)	8.7*	4	3
Effluent Flow Rate - After 2 Weeks (drops/sec)	--	4	7.5

*Channel developed in sand, test discontinued.

runs carried out, and illustrate that the precipitates formed in the acid mine water do, in fact, seek out the drainage channels and plug them. They also show that plugging with precipitates formed using only hydrated lime is more susceptible to subsequent channeling than for those resulting from the addition of limestone as well. The limestone does not yield as voluminous a precipitate and hence, being of greater density, is not as apt to develop a channel. The reduction in flow rate is not as great as in the vertical test for a comparable time, but limestone is effective enough to reduce a flow of 400 to 450 ml/min to a flow of drops.

In evaluating the test data from flow tests as described herein, it must be recognized that, because of the nature of the materials being tested and the reactions involved, different test runs can result in wide, yet insignificant, variations in flow rates, and flow rates during test runs extending over long periods of time can fluctuate widely. Therefore, the decision as to whether a given change in flow rate is significant is a subjective one that must be based on consideration of many factors, including results from other test runs.

SUMMARY

Results of these plugging tests indicate that precipitates resulting from the neutralization of acid mine water, while being bulky, are also capable of plugging the voids in a porous obstruction through which the water must pass. If the precipitate is excessively bulky, as with the addition of hydrated lime, there is the possibility that it might pass through the pores of the obstruction, but if this occurs, adding limestone for a short period results in a less bulky precipitate which will tend to plug up any channel that develops.

It appears that the most useful test is the vertical dynamic plugging test, from the standpoint of testing possible additives for injection into the acid mine water. The horizontal test is useful, but takes more time to set up and perform.

TEST 4

STUDIES TO OPTIMIZE SIZING OF FEED MATERIALS AND COMPOSITION VERSUS PRECIPITATE BULKING

To determine the most efficient utilization of the neutralization reaction and resultant precipitation of metallic ions from the water, studies were conducted in which the particle size of the additive material, the solids content of the slurry, and the quality of the water used to make up the slurry were varied.

LABORATORY PROCEDURE

For these studies, the bulking ratio test procedure described for Test 2 was used. Results, however, are reported as volume of precipitate rather than the bulking ratio because the actual volume produced is more meaningful than bulking ratio in terms of precipitate formed in a mine adit.

EFFECT OF VARYING PARTICLE SIZE

A monohydrated dolomitic lime and a high-calcium hydrated lime were evaluated at addition levels of 0.5 g/l and 1.0 g/l, in the range of particle sizes available: high-calcium hydrated lime in two ranges (-325 mesh and +325 mesh); monohydrated dolomitic lime in three ranges (-324 mesh, -200 +325 mesh, and -100 +200 mesh). Results (see Table 4-1) for the high-calcium hydrated lime were inconclusive because of the limited ranges of particle sizes. In the case of the monohydrated dolomitic lime in three ranges (-324 mesh, -200 +325 mesh, and -100 +200 mesh). Results (see Table 4-1) for the high-calcium hydrated lime were inconclusive because of the limited ranges of particle sizes. In the case of the monohydrated dolomitic lime, the two finer ranges were superior to the coarser range. This effect was noted at both addition levels.

Next, a high-calcium limestone (100% -1/8-mesh material) and a high-calcium chemical hydrate (100% -30-mesh material) were crushed and screened into seven ranges for each material. The individual ranges were then evaluated at a dosage level of 2 g/l. Results are shown in Tables 4-2 and 4-3.

Table 4-2 indicates that, for limestone, a finer particle size is more efficient. The limestone must be ground to -200 mesh or finer for efficient utilization of its neutralizing power, because the calcium sulfate formed in the reaction is deposited as a hard coating on the limestone particles and prevent further reaction of the stone with the acid. A smaller particle size initially exposes more surface to the acid water and therefore permits a higher proportion of the limestone to react.

Table 4-1 - Comparison of Solution pH and Volume of Precipitate Produced by Addition of High-Calcium Hydrated Lime and Monohydrated Dolomitic Lime, as a Water Slurry, to Synthetic Acid Mine Water - Effect of Varying Particle Size

Additive Material	Size Range (Mesh)	Dosage = 0.5 g/l		Dosage = 1.0 g/l	
		pH	Volume of Precipitate (ml)	pH	Volume of Precipitate (ml)
High-Calcium Hydrated Lime	-325	5.5	125	5.5	110
	+325	5.5	130	5.5	120
Monohydrated Dolomitic Lime	-325	5.0	75	5.5	180
	-200 +325	5.0	70	5.5	110
	-100 +200	4.5	20	5.0	40

Table 4-3 indicates that fineness of grind is not as critical for high-calcium chemical hydrate as it is for limestone. This is due to the fact that a chemical grade of hydrated lime, as used in this test, is a high-quality product from which coarse uncalcined or poorly calcined particles have been removed by screening after hydration. A hydrated lime whose screen analysis indicates the presence of coarse uncalcined particles would not be a true hydrated lime and, hence, would behave more like a limestone.

EFFECT OF VARYING SLURRY CONCENTRATION

The next variable of interest is the slurry concentration; the percent solids. The specific grades of locally available limestones and limes (the characteristics of which are shown in Tables 2-4 and 2-5) were evaluated at five slurry concentrations ranging from 1% to 50% solids. The dosage levels used for each material are based on achieving a pH of about 4, with the limestones pH 11 with the hydrated limes. Results obtained (shown in Table 4-4 and 4-5) indicate that within the limits of this evaluation, slurry concentration does not appear to influence the effectiveness of the reactant. However, differences for some of the materials seem to indicate that the dosage level may have a bearing on the effectiveness of utilization. A much more extensive evaluation would be required to derive more conclusive data.

Table 4-2 - Comparison of Solution pH and Volume of Precipitate Produced by Addition of High-Calcium Limestone, as a Water Slurry, to Synthetic Acid Mine Water - Effect of Varying Particle Size

Size Range (Mesh)		pH	Volume of Precipitate (ml)
-400		5.1	20
-325	+400	5.1	25
-200	+325	4.0	20
-100	+200	3.8	< 10
-20	+100	3.8	< 10
-8	+20	3.2	< 10
-4	+8	3.1	Original Lumps

NOTES: Material Added: Gold Bond #20, Ground and Screened
Dosage Level: 2 g/l
Slurry Concentration: 4% Solids

Table 4-3 - Comparison of Solution pH and Volume of Precipitate Produced by Addition of High-Calcium Hydrated Lime, as a Water Slurry, to Synthetic Acid Mine Water - Effect of Varying Particle Size

Size Range (Mesh)		pH	Volume of Precipitate (ml)
-400		11.2	70
-325	+400	11.0	75
-200	+325	10.7	75
-140	+200	10.6	75
-100	+140	11.0	70
-70	+100	10.7	60
-50	+70	11.0	60

NOTES: Material Used: Bell Mine Chemical Hydrate
Dosage Level: 2 g/l
Slurry Concentration: 4% Solids

Table 4-4 - Comparison of Volume (ml) of Precipitate Produced by Specific Grades Limestones and Hydrated Limes When Added as a Water Slurry in Synthetic Acid Mine Water - Effect on Varying Slurry Concentration

Slurry Concentration	Pulverized Limestone								Hydrated Lime			
	Code 55 Limestone at 4 g/1	Dry CAL-AG at 3 g/1	Gold Bond #10 PLS at 1 g/1	Gold Bond #10 PLS at 4 g/1	Bell Mine #90 PLS at 1 g/1	Pennsylvania #1 Stone at 3 g/1	Asphalt Filler at 1 g/1	Agricultural Limestone at 1 g/1	Washington Chemical Hydrate at 2 g/1	Chemical Hydrated Lime at 3 g/1	Bell Mine Chemical Hydrated Lime at 5 g/1	New Enterprise Hydrated Lime at 5 g/1
1	20	60	25	35	35	<10	20	40	40	60	70	45
5	20	40	20	40	30	10	15	25	70	50	60	50
10	20	45	20	25	30	10	15	20	60	50	50	50
25	20	40	20	40	30	10	10	25	50	50	50	50
50	20	40	20	30	30	10	15	20	50	50	50	50

Table 4-5 - Comparison of pH Resulting From the Addition of Specific Grades of Limestones and Hydrated Limes Injected as a Water Slurry to Synthetic Acid Mine Water - Effect of Varying Slurry Concentration

Slurry Concentration (% solids)	Pulverized Limestone								Hydrated Lime			
	Code 55 Limestone at 4 g/l	Dry CAL-AG at 3 g/l	Gold Bond #10 PLS at 1 g/l	Gold Bond #10 PLS at 4 g/l	Bell Mine #90 PLS at 1 g/l	Pennsylvania #1 Stone at 3 g/l	Asphalt Filler at 1 g/l	Agricultural Limestone at 1 g/l	Washington Chemical Hydrate at 2 g/l	Chemical Hydrated Lime at 3 g/l	Bell Mine Chemical Hydrated Lime at 5 g/l	New Enterprise Hydrated Lime at 5 g/l
1	3.7	4.0	4.0	4.9	5.0	3.5	3.8	4.4	10.8	11.5	11.7	11.5
5	3.4	3.8	3.8	4.7	3.9	3.3	3.9	4.0	9.9	11.1	11.4	11.4
10	4.0	4.2	4.3	5.0	3.7	3.2	3.9	3.9	10.3	10.9	11.6	11.5
25	4.0	3.9	3.9	5.0	3.7	3.4	3.8	4.0	10.3	10.6	11.5	11.2
50	3.6	3.7	3.8	4.8	3.6	3.1	3.9	3.7	9.8	11.0	10.6	11.4

EFFECT OF VARYING QUALITY OF WATER USED TO PREPARE SLURRY

The third variable studied was the quality of water used to prepare the slurry. Pure water would not normally be available to make up the slurry at the field site, and the mine effluent or a nearby stream would have to be used. However, as the treatment of the mine water proceeded, the quality of the water would change.

Therefore, on the first day of this evaluation both deionized water and synthetic acid mine water were used to make up the slurry to perform the bulking ratio test, using the four locally available hydrated limes. On the following day the test was repeated, this time using supernatant liquid from the first day's series of eight tests to make up the respective slurries. Results are shown in Table 4-6.

When deionized water with a pH of 7 was used, the final pH at 18 hours ranged from 11.1 to 11.3. However, when synthetic acid mine water with a pH of 3 was used, the final pH at 18 hours ranged from 10.0 to 11.5. This indicates that at startup pure water would be more desirable than acid mine water. However, comparison of the data for the second set of tests (performed with slurries made up with water that had been treated the day before) shows that all eight tests resulted in a solution pH within the narrow range of 10.9 to 11.5. Also, a comparison of data for the specific limes shows that after the first day's treatment, subsequent treatment is independent of the quality of the water used at startup.

SUMMARY

These studies indicate that: (1) particle size of the slurry solids is important for limestone, not so critical in the case of a good quality, correctly calcined and slaked hydrated lime, except as an indication of quality; (2) slurry concentration is not critical, provided a good dispersion is obtained; and (3) quality of water used to make up the slurry is not critical, especially after the water treatment has been started.

For purposes of the demonstration at the mine site, the limestone used will be specified in the size range of 200 to 400 mesh when its function is to take part in the neutralization reaction, and coarser when it is used as a particulate filler. The hydrated lime used will be specified in the size range of 140 to 400 mesh to assure a good quality material. The slurry concentration will be limited to a maximum of 5% to assure adequate dispersion of the solids. The water used for making up the slurry will be mine drainage water.

Table 4-6 - Comparison of Solution pH and Volume of Precipitate Produced by Addition of High-Calcium Hydrated Lime, as a Water Slurry, to Synthetic Acid Mine Water

Water Used to Prepare Slurry	Starting pH	Washington Chemical Hydrate (at 2 g/l)			Chemical Hydrated Lime #26 (at 3 g/l)			Bell Mine Chemical Hydrated Lime (at 5 g/l)			New Enterprise Hydrated Lime (at 5 g/l)		
		pH		Precipitate Volume (ml)	pH		Precipitate Volume (ml)	pH		Precipitate Volume (ml)	pH		Precipitate Volume (ml)
		Initial	18 hr		Initial	18 hr		Initial	18 hr		Initial	18 hr	
Deionized Water	7	11.7	11.1	60	12.0	11.2	60	11.9	11.3	70	12.0	11.1	65
Synthetic Acid Mine Water	3	10.0	10.0	85*	10.5	10.4	70	11.3	10.7	65	11.9	11.5	65
Decantate from Deionized Water Test	11.1-11.3	11.5	10.9	55	11.7	11.1	60	11.2	10.9	55	11.5	11.3	60
Decantate from SAMW Test	10.0-11.5	11.7	10.9	55	11.7	11.1	55	11.5	10.9	55	11.6	11.5	60

* Probably high due to experimental limitations of test method.

TEST 5

EFFECT OF AIR AGITATION ON BULKING RATIO AND ON PLUGGING CHARACTERISTICS

The purpose of introducing air into the acid mine water is to convert iron from the ferrous state to the ferric state so that the iron precipitation will start at a lower pH. If all the iron were converted to the ferric state, it could all be precipitated without having to raise the pH above 8. Therefore, the conversion of ferrous ions to ferric would result in a greater volume of precipitate. However, this increase is offset to some degree by the fact that the ferric oxide hydrate precipitates are denser than the ferrous oxide hydrate precipitates. Thus, while all of the iron would be precipitated at the lower pH, the increase n volume of precipitate, if any, would not be comparable to the precipitation of that same iron as ferrous oxide hydrate at the higher pH.

LABORATORY PROCEDURE

The effects of air agitation to the bulking properties and plugging properties were studied. Bulking was evaluated using the bulking ratio test described for Test 2, performed with and without a 5-minute period of air agitation, at several dosage levels of high-calcium limestone. The air was introduced by inserting a rubber hose attached to a pump (such as that used to aerate fish aquaria) into the water contained inthe cylinder, and bubbling air up through the water. The test was also performed varying the air agitation period for a fixed dosage level of high-calcium limestone. Plugging was evaluated using the static plugging test described for Test 3, performed with and without a 5-minute period of air agitation, at several dosage levels of high-calcium hydrated lime.

RESULTS

Results of the bulking tests (shown in Tables 5-1 and 5-2) indicate that the use of air does not appreciably affect the volume of precipitate. These tests were done with high-calcium limestone, which can only raise the pH to 5. Apparently, the lengths of time used for air agitation were insufficient to effect any large-scale conversion from ferrous to ferric.

Results of the plugging tests (shown in Table 5-3) indicate that air agitation is helpful in some instances. At a dosage level of 2.5 grams of high-calcium hydrate lime per liter of mine water, there was an appreciable decrease in percolation rate through the sand in the air-agitated test compared with the test with no air agitation.

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SUMMARY

Air agitation may be beneficial under certain conditions in connection with plugging a drainage opening. From a bulking standpoint, air agitation does not appear to be useful and may even be detrimental to achieving as high a bulking ratio as possible.

The tests would indicate, and other investigators have published supporting confirmation, that the ferrous to ferric conversion proceeds slowly at low pH and more rapidly at higher pH. Hence, at low pH, air agitation would have to be continued for a much longer period of time than at high pH for the same degree of conversion of ferrous to ferric.

Table 5-1 - Effect of Aeration on Precipitation Resulting From the Addition of Varying Quantities of High-Calcium Limestone to Synthetic Acid Mine Water

Weight of Additive (g/1)	Volume of Precipitate After 18 hours (ml)	
	With 5 Minutes Air Agitation	No Air Agitation
0.1	<< 5	<< 5
0.2	<< 5	<< 5
0.5	< 5	< 5
1.0	10	10
3.0	15	20
5.0	15	20

Table 5-2 - Effect of Varying Time of Air Agitation on Precipitation Resulting From the Addition of High-Calcium Limestone to Synthetic Acid Mine Water

Time Duration of Air Agitation (min)	Volume of Precipitate After 18 hours (ml)
5	10
8	10
10	10
15	15
20	15

Note: Dosage Level = 1 g/l

Table 5-3 - Effect of Aeration on Plugging Effectiveness of Precipitates Resulting from the Addition of Varying Quantities of High-Calcium Hydrated Lime to Synthetic Acid Mine Water

Weight of Additive (g/1)	Time for Flow of 100 ml, at 44 Foot Head (min)		Discharge pH	
	With 5 Minutes Air Agitation	No Air Agitation	With 5 Minutes Air Agitation	No Air Agitation
0.5	5.5	16.0	5	5
1.5	20.0	19.0	13	10
2.5	38.0	20.0	13	12.5
3.5	33.0	35.0	13	13
Control (Water Alone)	0.05		3	

TEST 6

EFFECT OF STATIC HEAD ON PLUGGING CHARACTERISTICS

If it is assumed that precipitates formed underground in acid mine water can effectively reduce the mine effluent flow by filling the voids in a drainage, the question remains whether this sealed barrier will remain watertight at an increased pressure and, if not, at what pressure the seal will break down.

LABORATORY PROCEDURE

The vertical dynamic plugging test was used in this study, except that the glass tube was replaced by a steel tube, so as to withstand the anticipated applied pressure. The additive used was Washington Chemical Hydrated Lime, added as a 2% water slurry. When the flow of mine water through the barrier was reduced from the initial 545 ml/min to a rate of 1 drop/sec, the time required as noted and the flows of mine water and slurry were stopped. After 18 hours, the time between drops was noted. The inlet end of the tube was then pressurized to 4.3 psig (corresponding to 10 feet of water). The time between drops was noted. The pressure was then increased to 8.7 psig (corresponding to 20 feet of water) and the time between drops noted. This was repeated, progressively increasing the pressure, until the flow could be measured in ml/min, or until the effluent end blew out.

RESULTS

The results, shown in Table 6-1, indicate that the initial slight pressurization increases the water flow somewhat; however, further increases in pressure increase the flow only slightly. A pressure is reached where the seal becomes porous. At this point, the flow increases markedly.

SUMMARY

The tests indicate that the seal formed as the precipitate in the acid mine water plugs the voids in the drainage channel does not become porous as the pressure is increased until a substantial pressure (corresponding to approximately a 100-foot head of water) has been reached. This is for a seal which is relatively "fresh" and formed from a single injection of additive. If we assume that additional precipitate, formed with the additional injection of additive, flows to reinforce the precipitate already in the voids, it is conceivable that the seal will be able to hold much higher pressures. Additional testing would be required in this area.

Table 6-1 - Effectiveness of Seal Under Increasing Pressure

Startup Phase				
		Test 1	Test 2	Test 3
Initial Acid Mine Water Flow Rate, ml/min			545	
Washington Chemical Hydrate (added as 2% water slurry) (g/l)			1.73	
Time to reduce flow to 1 drop/sec (min)		5	5	6
Time between drops at 18 hrs (sec)		32.0	45.0	10.0
Pressure Phase				
Pressure (psig)	Equivalent Head of Water* (ft)	Time Between Drops (sec)		
0	0	32.0	45.0	10.0
4.3	10	5.6	7.0	6.0
8.7	20	5.8	5.2	4.0
13.0	30	6.2	4.1	3.8
17.3	40	5.0	4.6	3.9
21.7	50	5.4	3.1	3.4
32.5	75	4.1	3.0	3.4
43.4	100	1.0	2.2	3.4
65.0	150	264**	2.7	2.8
86.7	200	790**	3.0	2.4
108.4	250	---	***	>700**
130.1	300	---	---	---

* Does not include 4-foot water column in tube.
** ml/min flow rate.
*** Effluent end blew out.

TEST 7

COMPOSITION OF ACID MINE WATER WHICH CAN BE TREATED EFFECTIVELY

Because of the wide range of composition of acid mine waters, the neutralization of a specific acid mine water might present a problem. Therefore, a study was conducted to determine whether limitations might prevent the treatment of some acid mine waters.

A range of synthetic mine waters was prepared containing varying concentrations of iron (Fe^{++}) ions and sulfuric acid representative of the metal ions and acidity encountered in acid mine waters. These waters were then neutralized using high-calcium hydrated lime and limestone. The volume of precipitate formed and the pH of the solution were used to evaluate the effectiveness of the treatment.

LABORATORY PROCEDURE

A series of 12 synthetic mine waters, in which the iron concentration was set at four levels, while the sulfuric acid concentration was set at three, was prepared. All other mineral constituents that might be encountered in actual acid mine waters were neglected in this study on the assumption that they would probably be present in relatively small quantities and their effects would be minor.

The respective concentrations of iron and acid and the corresponding calculated total acidity are shown in Table 7-1.

The initial pH of each of the 12 synthetic mine waters was first measured; the 950 milliliters of each water were placed in a separate graduated cylinder. A 6% slurry (3 g/50 ml) of a high-calcium limestone in deionized water was added to each of the cylinders. The cylinders were allowed to stand undisturbed for 18 hours, the solution pH was measured, and the volume of precipitate noted. One gram of the limestone was then added to each of the cylinders (after first slurrying it with 50 milliliters of solution from the cylinder). The cylinders were allowed to stand undisturbed for 24 hours, and the pH and volume of precipitate were noted. This procedure was repeated daily until 12 grams of limestone had been added to each cylinder. Results of this series are shown in Tables 7-2 through 7-4.

This series of tests was then repeated using a high-calcium hydrated lime as the additive except that the first addition was 1 gram in 50 milliliters rather than 3 grams in 50 milliliters as in the case of limestone. Also, when the pH in any cylinder was raised to more than 12, no further addition of lime was made to that cylinder. Results of this series are shown in Tables 7-5 through 7-7.

Table 7-1 Composition of Synthetic Mine Waters

Experimental Water No.	Fe^{++} (mg/l)	H_2SO_4 (mg/l)	Due to Fe^{++} (mg/l)	Free (due to H_2SO_4) (mg/l)	Total (mg/l)
1	100	1,000	179	1,020	1,199
2	1,000	1,000	1,790	1,020	2,810
3	5,000	1,000	8,950	1,020	9,970
4	10,000	1,000	17,900	1,020	18,920
5	100	5,000	179	5,100	5,279
6	1,000	5,000	1,790	5,100	6,890
7	5,000	5,000	8,950	5,100	14,050
8	10,000	5,000	17,900	5,100	23,000
9	100	10,000	179	10,200	10,379
10	1,000	10,000	1,790	10,200	11,990
11	5,000	10,000	8,950	10,200	19,150
12	10,000	10,000	17,900	10,200	28,100

In the reaction $H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2CO_3$:

1 mol of $H_2SO_4 \rightleftharpoons$ 1 mol of $CaCO_3$

or 98 # $H_2SO_4 \rightleftharpoons$ 100 # $CaCO_3$

$\therefore$ 100 mg/l $H_2SO_4 \rightleftharpoons$ 102 mg/l $CaCO_3$

In the reaction $FeSO_4 + CaCO_3 + H_2O \rightarrow FeO + CaSO_4 + H_2CO_3$:

1 mol of Fe^{++} (equivalent to 1 mol of $SO_4^{=}$) $\rightleftharpoons$ 1 mol of $CaCO_3$

or 56 # $Fe^{++} \rightleftharpoons$ 100 # $CaCO_3$

$\therefore$ 100 mg/l $Fe^{++} \rightleftharpoons$ 179 mg/l $CaCO_3$

Total acidity is the sum of the free acidity (due to the H_2SO_4) and the acidity due to the iron ($FeSO_4$)

Table 7-2 - Neutralization of Range of Acid Mine Waters
With High-Calcium Limestone - 1,000 mg/1 H_2SO_4
(Synthetic Mine Waters 1 through 4)

Total Weight of Additive (grams)	100 mg/1 Fe^{++} TA = 1,199		1000 mg/1 Fe^{++} TA = 2,810		5000 mg/1 Fe^{++} TA = 9,970		10,000 mg/1 Fe^{++} TA = 18,920	
	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)
0	2.0	0	2.0	0	2.0	0	2.0	0
3	4.0	<10	4.0	<10	4.0	12	4.0	20
4	6.0	10	5.0	<10	4.0	15	4.0	25
5	6.0	10	5.5	<10	4.5	15	4.0	25
6	7.0	10	5.5	10	4.5	15	4.0	30
7	7.0	10	5.5	15	4.5	20	4.0	30
8	7.0	10	6.0	15	4.5	25	4.0	30
9	7.0	10	6.0	20	4.5	30	4.5	30
10	7.0	10	6.5	20	5.0	30	4.5	30
11	7.5	15	6.5	20	5.0	30	4.5	30
12	7.5	15	7.0	20	5.5	30	5.0	30

Table 7-3 - Neutralization of Range of Acid Mine Waters With High-Calcium Limestone - 5,000 mg/1 H_2SO_4 (Synthetic Mine Waters 5 through 8)

Total Weight of Additive (grams)	100 mg/1 Fe^{++} TA = 5,279		1000 mg/1 Fe^{++} TA = 6,890		5000 mg/1 Fe^{++} TA = 14,050		10,000 mg/1 Fe^{++} TA = 23,000	
	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)
0	1.0	0	1.0	0	1.0	0	1.0	0
3	4.0	<10	4.0	<10	4.0	<10	4.0	<10
4	4.5	<10	4.0	<10	4.0	20	4.0	<10
5	6.0	20	5.5	15	5.5	40	5.5	20
6	6.0	30	6.0	20	6.0	40	5.5	30
7	6.0	35	6.0	30	6.0	40	5.5	40
8	6.0	40	6.0	30	6.0	40	6.0	40
9	6.0	40	6.0	30	6.0	40	6.0	40
10	6.5	40	6.0	35	6.0	45	6.0	40
11	6.5	40	6.0	40	6.0	45	6.0	40
12	6.5	40	6.0	40	6.0	50	6.0	40

Table 7-4 - Neutralization of Range of Acid Mine Waters
With High-Calcium Limestone - 10,000 mg/1 H_2SO_4
(Synthetic Mine Waters 9 through 12)

Total Weight of Additive (grams)	100 mg/1 Fe^{++} TA = 10,379		1000 mg/1 Fe^{++} TA = 11,990		5000 mg/1 Fe^{++} TA = 19,150		10,000 mg/1 Fe^{++} TA = 28,100	
	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)
0	<1.0	0	<1.0	0	<1.0	0	<1.0	0
3	2.0	<10	2.0	<10	2.0	<10	2.0	<10
4	2.0	10	2.0	<10	2.0	<10	2.0	<10
5	2.5	40	2.0	30	2.0	30	2.5	50
6	3.5	95	2.0	120	2.0	135	3.0	130
7	4.5	120	2.5	130	3.0	140	4.0	130
8	6.0	130	3.5	150	4.0	180	4.5	130
9	6.0	140	4.5	150	4.5	180	4.5	140
10	6.0	140	5.5	160	5.0	180	4.5	140
11	6.0	145	6.0	160	5.5	180	4.5	140
12	6.0	145	6.0	160	5.5	180	5.0	145

Table 7-5 - Neutralization of Range of Acid Mine Water With High-Calcium Hydrated Lime - 1,000 mg/1 H_2SO_4 (Synthetic Mine Waters 1 through 4)

Total Weight of Additive (grams)	100 mg/1 Fe^{++} TA = 1,199		1000 mg/1 Fe^{++} TA = 2,810		5000 mg/1 Fe^{++} TA = 9,970		10,000 mg/1 Fe^{++} TA = 18,920	
	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)
0	2.0	0	2.0	0	2.0	0	2.0	0
1	6.0	20	5.0	65	3.0	50	5.0	60
2	11.0	45	8.0	160	6.0	260	6.0	160
3	>12.0	20	11.0	140	6.0	290	6.0	230
4	-	-	>12.0	140	9.0	290	8.5	370
5	-	-	-	-	11.5	400	11.5	420
6	-	-	-	-	>12.0	370	>12.0	640

Table 7-6 - Neutralization of Range of Acid Mine Waters With High-Calcium Hydrated Lime - 5,000 mg/1 H_2SO_4 (Synthetic Mine Waters 5 through 8)

Total Weight of Additive (grams)	100 mg/1 Fe^{++} TA = 5,279		1000 mg/1 Fe^{++} TA = 6,890		5000 mg/1 Fe^{++} TA = 14,050		10,000 mg/1 Fe^{++} TA = 23,00	
	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)
0	1.0	0	1.0	0	1.0	0	1.0	0
1	2.0	0	2.0	0	2.0	0	2.0	0
2	4.0	5	3.0	20	2.0	20	2.0	25
3	5.0	10	5.0	50	3.0	50	3.0	55
4	8.5	55	8.5	60	5.5	140	4.0	140
5	11.5	80	11.0	250	9.0	260	8.0	250
6	>12.0	75	>12.0	200	>12.0	380	11.0	440
7	-	-	-	-	-	-	>12.0	630

Table 7-7 - Neutralization of Range of Acid Mine Waters With High-Calcium Hydrated Lime - 10,000 mg/1 H_2SO_4 (Synthetic Mine Waters 9 through 12)

Total Weight of Additive (grams)	100 mg/1 Fe^{++} TA = 10,379		1000 mg/1 Fe^{++} TA = 11,990		5000 mg/1 Fe^{++} TA = 19,150		10,000 mg/1 Fe^{++} TA = 28,100	
	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)	pH	Vol of PPT (ml)
0	<1	0	<1	0	<1	0	<1	0
1	1.0	0	1.0	0	1.0	0	1.0	0
2	2.0	5	2.0	0	2.0	0	2.0	5
3	2.5	20	2.0	5	2.0	20	2.0	20
4	3.0	60	2.5	30	2.5	40	2.0	50
5	>12.0	130	3.0	40	3.0	50	3.0	80
6	-	-	12.0	210	3.0	530	3.0	530
7	-	-	>12.0	240	12.0	690	11.5	710
8	-	-	-	-	>12.0	720	>12.0	790

RESULTS

The data shown in Tables 7-2 through 7-7 indicate that if a sufficient amount of additive is used, all the synthetic mine waters in the range studied could be neutralized. However, the effectiveness of the neutralization to precipitate the mineral content is not the same for all the waters studied. Also, the neutralization reaction does not proceed along a predicted curve, but rather is influenced by the buffering action of the mineral content. In many cases, successive additions of limestone or lime do not increase the pH, until a point is reached when the addition of "one more gram" results in a large increase in pH. When these tests were started, it was hoped that plots of the different variables could be prepared; however, this could not be done because of their limited scope.

As expected, the waters with the higher iron content yielded higher volumes of precipitates; however, the increase in volume was not as great as might be expected. For example, referring to Table 7-5, the water containing 100 mg/l Fe^{++} yielded a total precipitate volume of 45 milliliters at a pH of 11, for an addition of 2 grams of hydrated lime. The water containing 100 mg/l Fe^{++} yielded a total precipitate volume of 140 milliliters at a pH of 11, for an addition of 3 grams of hydrated lime. There was not a tenfold increase in volume of precipitates for a tenfold increase in iron content. This phenomenon is due in part to the fact that precipitation of iron hydroxides from iron sulfate solutions is a highly complex reaction, depending on the formation of numerous complexes of iron oxides associated with varying quantities of water. Part of this phenomenon is also due to the presence of free acidity, as shown by a comparison of 100 mg/l Fe^{++} water in Tables 7-5, 7-6, and 7-7. Increasing the free acidity of the water required more hydrated lime to raise the pH to any given level, but when that pH had been reached, the volume of precipitate was much higher.

SUMMARY

The precipitation of the metallic iron content of acid mine waters, especially iron, during the neutralization is a complex reaction, depending on many variables. Part of this complexity is the multitude of forms in which the iron oxide hydrates can exist, both in themselves and when precipitated in the presence of other metal ions. The results of these two series of tests indicate that any water whose analysis falls within the wide range of acid mine waters encountered can be treated effectively. The degree of effectiveness, and other specific variables, can only be determined in the field for waters that are actually encountered. More definitive data would require a test program of greater scope than the contract will allow.

TEST 8

GELLING OF ACID MINE WATER WITH SYNTHETIC GELLING AGENTS

Another approach to underground precipitation in acid mine water is that of gelling the water to form either a rigid or semirigid solid. There are numerous materials that can gel a mass of water; the problem is the introduction of the gelling material into the water external to the mine adit without gelling taking place until after the mixed water is returned to the mine voids so that the gel is formed underground. A material that appears to be appropriate for this use is cellulose gum, marketed as CMC-7H by Hercules, Inc. This gum increases the viscosity of water. In addition, if ions of heavy metals (such as aluminum or iron) are introduced over an extended period of time, extensive cross-linking occurs; the ions enter the structure and make the gels rigid.

LABORATORY PROCEDURE

The manufacturer's recommended procedures were followed during the laboratory evaluation of this gum in an attempt to reproduce the expected results. Starting with deionized water, aluminum ions were added in the form of aluminum acetate. After thorough dispersion, the cellulose gum was added and dispersed by hand. Four tests that varied the aluminum ion content and amount of cellulose gum were performed.

Synthetic mine water with an iron and aluminum content was then substituted for the deionized water. No more ions of heavy metal were added. Cellulose gum was then added and dispersed by hand. After 3 hours, the tubes were evaluated for gelling.

The entire series of seven tests was repeated. In the second series, good dispersion was accomplished with the use of a blender.

RESULTS

Results of these tests are shown in Table 8-1. The first four tests (in which deionized water and aluminum acetate were used) were performed to confirm the manufacturer's literature. The results, while not verifying the manufacturer's results, were close enough to indicate that the minor differences could easily have been caused by experimental variations. The main point to remember in using this cellulose gum is that the gelling is largely dependent on the dispersion of the gum and the heavy metal ions required for cross-linking. Where mixing was good, the formation of rigid gels occurred as expected, though faster than anticipated. Poor mixing resulted in high concnetrations of either gum or ions which, in turn, resulted in rigid gels in some portions of the tests cylinder and no gels in other portions. The tests confirmed the need for the proper concentrations to achieve the desired degree of rigidity, and the proper dispersion to achieve the desired concentrations.

The last three tests (in which mine water was used) were performed to determine whether the naturally occurring heavy metal ions could be used to cross-link the gum and form a rigid gel. Three ratios (ranging from 0.2 to 1.0%) of gum synthetic mine water were tried. As before, results from poor mixing could not be evaluated, other than to confirm the necessity for good mixing. Results from the well-mixed series indicated that 0.2% is too low to produce gel; 0.5% resulted in a soft gel witin a 24-hour period; and 1.0% resulted in a firm gel, formed too quickly. For synthetic water, the ideal concentration lies somewhere between 0.5 and 1.0%.

SUMMARY

The use of cellulose gum for gelling mine water appears to be feasible under the correct conditions; however, a great deal more laboratory work must be done before its proper application can be established. Its attractiveness from a cost standpoint would depend on the quantity used; its use appears to be limited to the gelling of mine water after the effluent drainage points have been plugged.

Table 8-1 - Gelling of Water by the Use of Cellulose Gum

Test No.	Water Used (ml)		Aluminum Acetate		CMC-7H		Gel* Time (hr)	Results	
	DW	AMW	Wt (g)	Conc. on CMC (%)	Wt (g)	Conc. on AMW (%)		Poor Mixing (by hand)	Good Mixing (by blender)
1	1000	-	2	20	10	1.0	1-1/2	Rigid gel formed at top of cylinder, instantly upon addition of gum. A precipitate then appeared at bottom of cylinder within approximately 10 minutes.	Uniform dispersion throughout - formed uniform rigid gel during mixing
2	1000	-	1	20	5	0.5	2	As in Test 1 above.	Firm gel with slight water layer at top of cylinder. Within 30 minutes the entire tube was filled with a rigid gel.
3	1000	-	0.35	7	5	0.5	24	Firm gel formed throughout 25% of the water within 24 hours.	Upon mixing formed very viscous liquid, which became a soft gel throughout within 24 hours.
4	1000	-	0.04	2	2	0.2	4	Immediate gel formed - in lumps. Within 4 hours a flexible, soft extension of the gel formed at top of cylinder. Gel filled approximately 5% of volume.	Formed a thickened liquid, but no gel formed within 4 hours.
5	-	1000	0	0	10	1.0	-	Firm gel resulted immediately which became rigid within 3 hours.	Firm gel formed while mixing, no change occurred thereafter.
6	-	1000	0	0	5	0.5	-	As in Test 5, above.	No gel formed within first several hours, very soft gel filled cylinder within 24 hours.
7	-	1000	0	0	2	0.2	-	Gel formed in single lump upon addition of gum - lumps became rigid after 3 hours.	No appreciable gelling or thickening occurred.

*Per manufacturer's literature.

TEST 9

COATING OF MINE SURFACES BY PRECIPITATES FORMED UNDERGROUND

It was postulated that precipitates formed underground in a mine adit might form a protective coating and prevent dissolution of the pyrites with the acid mine water. To explore this possibility, a number of samples, including pyrites, coal, and shale, were collected from the demonstration mine site and forwarded to the laboratory.

LABORATORY PROCEDURE

At the laboratory, the samples were placed in vats of synthetic acid mine water. The required amount of high-calcium hyrated lime in a 10% water slurry was added to the vats. The usual precipitates (whitish or graygreen) formed and clouded the entire container. Observations at 18 hours indicated a uniform fallout over the bottom of the containers and over the specimens. No precipitate adhered to the vertical surfaces; it tended to turn brown (indicating oxidation or the iron) after a period of several days.

After one week, the specimens were removed from the tank and examined. In general, the precipitate was easily washed away; however, where it was in contact with pyrites, it did not wash away and the presence of pyrites in the coal was clearly defined. But since the color of the precipitate at these points was reddish-orange (indicating a high concentration of ferric oxide), it appears that rather than sealing off the pyrites, the precipitate accelerated their oxidation. Therefore, precipitates formed underground in the acid mine water were eliminated from consideration for sealing in the coal or shale.

Furthermore, experimenters studying the reaction of groundwater seeping into an underground mine and becoming acidic (because of the dissolution of iron pyrites) have proven the importance of oxygen as the ultimate oxidant. From the results of their studies, it is apparent that most of the dissolution of pyrites takes place in adits not flooded with mine water; thus, coating the surfaces of flooded adits appears to be unbeneficial.

No further studies were made of coating mine surfaces as a deterrent to pollution from acid mine water.

CONCLUSION

It was concluded that the underground precipitation does not result in the formation of a protective coating on the pyrites particles.

TEST 10

AUGMENTATION OF MINERAL CONTENT BY ADDITION OF WASTE PICKLE LIQUOR

At times it might be desirable or necessary to augment the mineral content of acid mine water; therefore, the precipitation of such augmented mine water was studied. Waste pickle liquor (sulfate) was used as the additional source of mineral content because it is readily available, high in iron content, and presents a disposal problem in itself.

LABORATORY PROCEDURE

The bulking ratio test procedure described for Test 2 was used for this study. Three experimental waters were prepared by adding pickle liquor to the synthetic acid mine water to give ratios of acid water to waste pickle liquor of 99:1, 95:5, and 90:10. A control containing no waste pickle liquor was also used.

Waste pickle liquor from the Irwin Plant of the U.S. Steel Corporation was used in the tests and had an approximate composition as follows:

$FeSO_4$ 13.0% by weight

H_2SO_4 8.5% by weight

The iron concentration is approximately 50,000 mg/l; free acidity 87,000 mg/l; and total acidity 173,000 mg/l.

Four high-calcium hydrated limes were used, at the optimum addition level for each, to precipitate the mineral content of the water. The volume of precipitate and the pH of the solution were measured after 18 hours.

RESULTS

Results are presented in Table 10-1. The augmentation of the acid mine water with only 1% of waste pickle liquor produced, on the average, a doubling of the volume of precipitate. Augmentation with higher percentage of waste pickle liquor produced a decrease rather than an increase. This is due to the fact that the addition level of additive was not increased to neutralize the additional acidity due to the waste pickle liquor. Increasing the addition of lime would precipitate more of the mineral content as the pH is increased.

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Table 10-1 - Precipitation in Acid Mine Water Augmented With Waste Pickle Liquor

Ratio of Acid Mine Water to Waste Pickle Liquor	Washington Chemical Hydrate		Chemical Hydrated Lime #26		Bell Mine Chemical Hydrated Lime		New Enterprise Hydrated Lime	
	at 2 g/1		at 3 g/1		at 5 g/1		at 5 g/1	
	pH	Vol of Precipitate (ml)	pH	Vol of Precipitate (ml)	pH	Vol of Precipitate (ml)	pH	Vol of Precipitate (ml)
100:0 (control)	11.0	60	10.8	65	10.3	55	10.5	55
99:1	4.0	100	3.7	140	4.1	140	11.0	150
95:5	1.9	15	2.3	60	2.0	40	2.1	30
90:10	1.7	20	2.0	40	1.6	30	1.8	80

SUMMARY

Augmentation of the mineral content of acid mine water to produce additional volume of precipitate is feasible using waste pickle liquor (sulfate) from the steel industry. The additional acidity introduced by the waste pickle liquor increases the quantity of neutralizing additive required.

TEST 11

CONTINUOUS NEUTRALIZATION OF ACID MINE WATER

A third application of underground precipitation for abating pollution from abandoned coal mines is the continuous injection of a neutralizing agent(s) through boreholes located some distance back from the effluent point so that the mine water will be neutralized and the resultant sludge will remain in the mine.

LABORATORY PROCEDURE

The horizontal dynamic plugging test described for Test 3 was used, except that the tube sloped away from the effluent end rather than toward it. When slurry was injected through the borehole, the precipitate formed flowed away from the effluent end rather than toward it (if the flow of mine water was not great enough to overcome gravity and pull the precipitate up to the effluent end). The slope was adjusted to 1%, 5%, and 10%. In the first set of tests, the borehole was placed 4 inches back from the effluent end. Additional tests were then performed with the borehole placed 14 and 21 inches back.

RESULTS

Results of these tests are shown in Tables 11-1 through 11-3. In the first set of tests, reported in Table 11-1, the placement of the slurry inlet proved to be too close to the effluent end for two reasons: first, the high pH of the discharge stream for such a low additive level indicated insufficient neutralization time; second, the plugging of the sand barrier indicated insufficient distance for settling of the precipitate to the bottom surface of the tube, at which point it started to roll back down the tube.

In the tests reported in Tables 11-2 and 11-3, the slurry inlet was placed 14 and 21 inches back, respectively. These tests were carried out only until the precipitate had rolled back 50 cm; therefore, some of the tests were of very short duration. Because of the neutralization, the pH of the effluent stream was increased in every test. Some reduction in the flow was noted, but in no case was the flow reduced to a drop-by-drop rate. Flow back down the tube was very difficult to measure with any degree of accuracy. Nevertheless, it appears that, within the experimental limitations, there was a good correlation between the various tests.

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Table 11-1 - Precipitate Flow in Sloped Adit Resulting from Neutralization of a Flowing Stream of Acid Mine Water with a 2% Slurry of High-Calcium Hydrated Lime

Slurry Inlet: 4 Inches from Effluent End

		1% Slope		5% Slope		10% Slope	
Total Elapsed Time (min)	Total Slurry Added (ml)	Effluent Flow Rate (ml/min)	Effluent pH	Effluent Flow Rate (ml/min)	Effluent pH	Effluent Flow Rate (ml/min)	Effluent pH
0	0	900	3.0	900	3.0	900	3.0
2	50	900	11.5	800	11.5	875	11.5
4	100	735	11.5	560	11.5	740	11.5
6	150	400	11.5	135	11.5	530	11.5
8	200	250	11.5	5*	11.5	175	11.5
10	250	250	11.5	5*	11.5	160	11.5
12	300	200	11.5	5*	11.5	90	11.5
14	350	2*	11.5	5*	11.5	50	11.5
16	400	2*	11.5	5*	11.5	-	-
18	450	2*	11.5	5*	11.5	-	-
Time for Precipitate to Flow Back 50 cm (min)		16.27		9.67		3.17	
Linear Flow Rate of Precipitate Back Down Tube (ft/min)		0.101		0.170		0.517	

* drops/sec

Table 11-2 - Precipitate Flow in Sloped Adit Resulting from Neutralization of a Flowing Stream of Acid Mine Water with a 2% Slurry of High-Calcium Hydrated Lime

Slurry Inlet: 14 Inches from Effluent End

		1% Slope		5% Slope		10% Slope	
Total Elapsed Time (min)	Total Slurry Added (ml)	Effluent Flow Rate (ml/min)	Effluent pH	Effluent Flow Rate (ml/min)	Effluent pH	Effluent Flow Rate (ml/min)	Effluent pH
0	0	900	3.0	900	3.0	900	3.0
2	50	228	3.5	522	3.1	396	3.4
4	100	486	3.2	444	3.4	-	-
6	150	372	3.3	384	3.3	-	-
8	200	240	3.3	292	3.6	-	-
10	250	132	3.9	192	3.5	-	-
12	300	-	-	-	-	-	-
14	350	-	-	-	-	-	-
16	400	-	-	-	-	-	-
18	450	-	-	-	-	-	-
Time for Precipitate to Flow Back 50 cm (min)		5.58		4.47		1.68	
Linear Flow Rate of Precipitate Back Down Tube (ft/min)		0.294		0.367		0.980	

Table 11-3 - Precipitate Flow in Sloped Adit Resulting from Neutralization of a Flowing Stream of Acid Mine Water with a 2% Slurry of High-Calcium Hydrated Lime

Slurry Inlet: 21 Inches from Effluent End

Total Elapsed Time (min)	Total Slurry Added (ml)	1% Slope		5% Slope		10% Slope	
		Effluent Flow Rate (ml/min)	Effluent pH	Effluent Flow Rate (ml/min)	Effluent pH	Effluent Flow Rate (ml/min)	Effluent pH
0	0	900	3.0	900	3.0	900	3.0
2	50	330	3.5	504	4.0	594	3.1
4	100	324	3.3	504	4.0	576	3.1
6	150	468	3.3	348	4.0	-	-
8	200	464	3.4	348	3.7	-	-
10	250	252	3.9	300	4.5	-	-
12	300	152	3.8	270	3.9	-	-
14	350	132	3.9	300	3.8	-	-
16	400	160	4.1	330	4.7	-	-
18	450	152	4.0	318	3.8	-	-
Time for Precipitate to Flow Back 50 cm (min)		*		7.75		2.45	
Linear Flow Rate of Precipitate Back Down Tube (ft/min)		0.025		0.212		0.67	

*7.62-cm flow in 10 minutes, then precipitate stopped flowing

SUMMARY

Results of these tests indicated the feasibility of continuous neutralization of acid mine drainage by injection of the slurry into the adit, and allowing the precipitate to flow back down the adit to lower portions of the mine. The success of this treatment depends on the slope of the mine adit (in relation to the flow rate of the acid mine water) and on the injection point being placed far enough from the effluent end to prevent forward flow of the precipitate. By varying the quantity and concentration of slurry, the pH of the effluent stream can be adjusted to any desired level. Additional laboratory work will be required to obtain more refined data; however, correlation of such laboratory work with field conditions would be difficult. Therefore, a small field demonstration, based on present laboratory tests, would be desirable as the next development step.

TEST 12

USE OF FLY ASH

Because of its low cost and widespread availability, fly ash from coal-burning power generating stations is of interest for possible use in connection with the underground precipitation concept. However, while slightly alkaline, fly ash cannot be considered as a neutralizing agent. Therefore, its use from a bulking standpoint (which depends upon the neutralization of the acid water with the formation of a bulky sludge as the mineral content precipitates of the water) does not appear promising.

The major value of fly ash appears to be its ability to enter into a reaction to form ettringite ($6\ CaO \cdot Al_2O_3 \cdot 3SO_4 \cdot 33\ H_2O$) when all the necessary reactants are present. This reaction is the basis for the substitution of fly ash for part of the cement to produce a concrete with superior properties over nonfly ash concretes. This indicates that fly ash is valuable in sealing drainage channels.

LABORATORY PROCEDURE

The composition and form of fly ash varies, depending on the types of fuel being burned and on the pretreatment of the fuel before being fired. The following fly ashes were included in the laboratory evaluation:

Fly Ash	Active Components		
	CaO	MgO	SO_3
Bituminous	Los	Low	Low
Desulfurization			
(Bituminous with High-Calcium Injection)	High	Low	High
American Lignite	High	High	Medium
European Lignite	Medium	Medium	Low

In addition, bituminous fly ash interblended with monohydrate dolomitic and bituminous fly ash interground with monohydrate dolomitic were included to represent fly ashes that have been modified to augment the content of reactants in which a fly ash might be deficient.

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Autogenous Hardening of Fly Ashes

To test the autogenous hardening of fly ash, glass cylinders (2 inches OD by 6 inches long) were capped at one end with nylon cloth held in place by a rubber band. These containers were filled and placed capped end down into a 2-1/2-gallon aquarium that was filled to a depth of 1 inch with deionized water. The aquarium was allowed to stand undisturbed for seven days, during which time water was absorbed into the fly ash. At the end of seven days, the force required for a 0.025-square-inch rod to penetrate 1 inch into each sample was measured. Results, shown in Table 12-1, indicate that certain fly ashes will harden when exposed to moisture.

The test was repeated using three 2-1/2-gallon aquariums. One sample of each fly ash was placed into each of the aquariums, which are filled to the depth of 1 inch with:

(1) Deionized water

(2) Synthetic (reconstituted) sea water

(3) Synthetic acid mine water

The aquariums were allowed to stand undisturbed for seven days. Penetration resistance was measured as before, then allowed to stand undisturbed for a total of 70 days, and the penetration resistance was measured again. Results shown in Table 12-2 again indicate that fly ashes will harden when exposed to moisture (water quality does not appear to be important), provided the reactants to form ettringite are present and sufficiently dispersed. Long-term data indicate that the hardening process produces extremely high penetration resistance and a slight expansion in the mass, as indicated by the cracking of a number of cylinders.

Bituminous fly ash, per se, does not contain sufficient quantities of reactants to harden by itself. Interblending bituminous fly ash with monohydrated dolomitic lime, while augmenting the CaO and MgO content, does not mix the reactants sufficiently to be effective. Because of the more intimate mixing of the reactants, intergrinding the two appears to be beneficial. The desulfurization fly ashes appear to have good hardening properties because of their high content of reactants resulting from the mixing of limestone with the coal before firing. American lignite showed good hardening properties because of its high content of CaO, MgO, and SO_3, while European lignite, with less CaO, MgO, and SO_3, did not harden at all.

Plugging Effectiveness of Fly Ashes

The hardening test indicated that when fly ash reacts to form ettingite, there is a slight expansion of the reaction mass. Thus the fly ash hardening reaction would be useful in plugging effluent drainage channels.

Table 12-1 - Autogenous Hardening of Fly Ashes
(Short-term Tests, Using De-Ionized Water)

Material	Chemical Analysis (%)						Penetration Force Required After 7 Days (psi)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_2	
Bituminous Fly Ash	38.5	23.6	25.7	3.7	1.1	1.2	9
Bituminous Fly Ash (90%) Interblended with Monohydrate Dolomitic (10%)	34.65	21.24	23.13	8.24	4.50	1.08	46
Bituminous Fly Ash (91%) Interground with Monohydrate Dolomitic (9%)	35.04	21.48	23.39	7.79	4.16	1.09	1075
Desulfurization Fly Ash (Calcite Injection)	25.8	9.7	14.3	40.4	0.8	6.8	1165
Desulfurization Fly Ash (Chalk Injection)	35.8	13.7	15.8	23.9	0.7	2.2	1256
North American Lignite	27.5	10.1	10.6	29.9	16.8	1.2	2152
European Lignite	30-35	15-20	15-20	10-15	3-5	0-3	26

Table 12-2 - Autogenous Hardening of Fly Ashes
(Long-term Tests, Using Various Waters)

Material	Moisture Source					
	De-Ionized Water		Synthetic Sea Water		Synthetic Acid Mine Water	
	Penetration Force (psi) Required After					
	7 Days	70 Days	7 Days	70 Days	7 Days	70 Days
Bituminous Fly Ash	0	0	0	0	0	0
Bituminous Fly Ash (90%) Interblended with Monohydrate Dolomitic (10%)	0	0	0	400	0	Negligible
Desulfurization Fly Ash (Limestone Injection)	0	5200	0	Cylinder Cracked	0	7200
Desulfurization Fly Ash (Chalk Injection)	600	> 8000	2000	> 8000	400	7880
North American Lignite	1600	> 8000	1800	3800	2200	Cylinder Cracked
European Lignite	0	0	0	0	0	0

The horizontal dynamic plugging test described for Test 3 was used to evaluate four fly ashes: bituminous fly ash, bituminous fly ash interblended with monohydrated dolomitic lime, desulfurization fly ash, and North American lignite fly ash. Results shown in Table 12-3 indicate that bituminous fly ash alone does not have any plugging properties (as would be expected since bituminous fly ash alone does not harden). The other three fly ashes were effective, even after being in place for 24 weeks.

Hardening of Lime/Fly Ash/Gypsum Mixtures

Since the formation of ettringite is responsible for the hardening of fly ash, and since ettingite is composed of CaO, Al_2O_3, and $CaSO_4$, the effect of gypsum ($CaSO_4$) supplementation to lime/fly ash mixtures was studied. The penetration test described above was used to determine the hardening of mixtures of various ratios of lime/fly ash/gypsum. Results, shown in Table 12-4, indicate that the addition of gypsum is beneficial, as evidenced by the cracking of 19 of the 48 tubes after 8 weeks, which was caused by the expansive forces of the reaction.

The samples with no addition of gypsum did not crack, indicating that the degree of reactivity is lower when no gypsum is included.

Stabilization of Acid Neutralization Sludges

The possibility of using fly ash to stabilize (harden) sludges resulting from the neutralization of acid mine waters was investigated. Sludges were prepared by treating a synthetic waste pickle liquor (150,000 mg/l SO_3 - and 10,000 mg/l Fe^{++}) with different limes to yield sludges having pH of either 7.2 or 12. After settling overnight, the decantate in each test was siphoned off and the sludge was mixed with bituminous fly ash (at varying ratios of sludge to fly ash). Each mixture was then water-cured, and the development of penetration resistance noted after 6 weeks.

Results shown in Table 12-5 indicate that bituminous fly ash can be used to solidify and harden sludges resulting from the neutralization of acid mine water. Note that the sludge resulting from the use of high-calcium hydrated lime to neutralize the acid mine water was not hardened by the fly ash, because of the absence of MgO. Although the formula for ettringite does not indicate the pressence of MgO, the data indicate that magnesium is beneficial, perhaps partially substituting for some of the CaO in the structure.

SUMMARY

It appears that the use of the fly ash in connection with the underground precipitation concept for abatement of pollution from acid mine

Table 12-3 - Plugging Effectiveness of Fly Ashes

Material	Flow (drops/sec) After								
	30 min	18 hr	2 days	3 days	1 wk	2 wk	5 wk	15 wk	24 wk
Bituminous Fly Ash	1.0	0.4	0.4	0.3	2.0	4.0	13	*	*
Bituminous Fly Ash (90%) Interblended with Monohydrate Dolomitic (10%)	2.0	0.7	0.5	0.4	0.3	0.3	0.2	**	**
Desulfurization Fly Ash (Calcite Injection)	1.0	0.6	3.3	1.7	67	93	1.0	1.0	0.5
North American Lignite	0.07	0.06	0.04	0.035	**	**	**	**	**

*Channel

**No drops (effluent rate less than evaporation rate)

Table 12-4 - Hardening of Lime/Fly Ash/Gypsum Mixtures
(Using Various Waters)

Blend Weight Ratios			Penetration Force Required After 8 Weeks (psi)					
			Interground Samples			Interblended Samples		
High-Calcium Hydrated Lime	Bituminous Fly Ash	Ground Gypsum	Deionized Water	Synthetic Sea Water	Synthetic Acid Mine Water	Deionized Water	Synthetic Sea Water	Synthetic Acid Mine Water
1	3	0	2480	6400	960	0	1200	400
1	12	0	840	1000	1600	Negligible	1600	600
1	3	1/2	2000*	2800*	2000*	3800	7600	> 8000
1	6	1/2	> 8000	3360*	1520*	3200	3800	6400
1	3	1	3200*	1400*	2200*	2000*	1600*	1600*
1	12	1	3200	1400	1360	No Test	No Test	No Test
1	3	2	1600*	1000*	1000*	3000*	2000*	600*
1	12	2	1600*	1600	3200	1800*	800	1600

*Cylinder Cracked

Table 12-5 - Stabilization of Acid Neutralization Sludges Formed from Acid Mine Water

Neutralizing Agent Used to Form Sludge	pH of Sludge	Wt. of Bituminous Fly Ash Added to 100 Grams of Sludge (g)	Penetration Resistance After 6 weeks (psi)
Monohydrate Dolomite	7.2	0	0
		5	0
		10	0
		20	0
		30	560
		50	960
	12.0	0	0
		5	0
		10	1000
		20	2200
		30	4400
		50	2400
High-Calcium Hydrate	7.2	0	0
		5	0
		10	0
		20	0
		30	0
		50	560
	12.0	0	0
		5	0
		10	0
		20	0
		30	0
		50	0

drainage is desirable, and opens many possibilities. However, its usefulness at a specific location will depend on a number of factors.

The usefulness of fly ash is determined by the reaction that produces the ettringite structure, and the accompanying expansive forces. Calcium, aluminum, and sulfate ions are necessary for this reaction. Magnesium is beneficial; apparently it replaces some of the calcium in the structure. Tests with acid mine water indicate that ferric iron can replace some of the aluminum in the resulting ettringite structure. All of the constituents are either present or readily available when acid mine water is treated with either the proper, or properly augmented, fly ash.

It does not appear to be desirable to include fly ash in the Phase II field demonstration at the Driscoll No. 4 Mine, at least initially, for the following reasons:

(1) The most readily available fly ash for this demonstration mine site is a bituminous fly ash from the Seward Station, operated by the Pennsylvania Electric Company, which would require calcium and magnesium augmentation. This would mean that hydrated dolomitic lime would be required for best results, and only high-calcium hydrated lime is available within a reasonable distance from the mine site. (Some magnesium ions are present in the mine water, but the concentration appears to be too low.)

(2) To obtain best results, the fly ash and lime would have to be interground, necessitating a mill at the site.

(3) Augmentation of the $CaSO_4$ content appears to be desirable, if not necessary, to increase the expansion forces during the reaction.

Funds permitting, fly ash could be used later in the program to plug one of the drainage effluent points that may develop as the water level rises in the mine after the successful plugging of the lower effluent point.